AFIT/GEE/ENV/99M-02

COST-BENEFIT ANALYSIS OF COSOLVENT FLUSHING TO TREAT GROUNDWATER CONTAMINATION SOURCE AREAS

THESIS

Stacey L. Anason, Capt, USAF

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Presented to the Faculty of the Graduate School of Engineering

Of the Air Force Institute of Technology

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering and Environmental Management

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Abstract

Dense non-aqueous phase liquids (DNAPLs) in the zone beneath the water table can be a virtually permanent source of groundwater contamination that cannot be remediated by currently available technologies. Cosolvent flushing is a new technology that has the potential to remediate these sites and could pose a solution to the problem of DNAPL source areas.

A computer model was developed to determine the cost and time to remediate an aquifer using cosolvent flushing. Included in the model is a module to calculate costs of recycling the alcohol that is used as the cosolvent. The model was validated using site conditions to a prior study. It was determined that recycling the cosolvent allows cosolvent flushing to be a cost effective alternative to surfactant flushing, another new technology being considered for DNAPL source area remediation.

Sensitivity analysis of the model was conducted by varying the saturation percentage of contaminant, percentage and type of alcohol used in the cosolvent mixture, site hydraulic conductivity, and the contaminant. Five alcohols were modeled: methanol, ethanol, 1-isopropanol, 2-isopropanol, and tert-butyl-alcohol (TBA). 1-Isopropanol, 2-Isopropanol, and TBA were always more expensive than methanol and ethanol. Methanol was found to be more cost-effective when used on DNAPLs with high solubilities, while ethanol was found to be more cost-effective when used on DNAPLs with low solubilities. Methanol always took longer than ethanol to remediate the source area since methanol had a lower cosolvency power.

Chapter 1
Introduction

1.1 Motivation

The Department of Defense (DoD) is responsible for cleaning up contamination at over 10,000 active sites at more than 700 military installations (Tennesen, 1993). The contamination was due mainly to the intentional or accidental disposal of hazardous wastes generated by military activity. Of the 700 military installations, 123 of the installations have sites that are on the Environmental Protection Agency's Superfund list of most hazardous (Tennesen, 1993). DoD has invested almost $15 Billion in its environmental restoration program through 1996 (Budget of the US, 1997) and it is estimated that an additional $15 billion will be required to cleanup all remaining DoD sites (Defense Restoration Program, 1997). The Air Force alone will require approximately $7.5 billion to remediate its remaining 2,121 sites (Defense Restoration Program, 1997).

Although the site conditions at each Air Force installation are unique, sites share common characteristics. The most common contaminants in the soil and groundwater beneath U.S. Air Force installations are petroleum hydrocarbon contaminants, such as benzene, toluene, and xylene; solvents, such as trichloroethylene; and toxic metals (Gorelick et. al., 1993). Typically organic contaminants such as petroleum hydrocarbons and solvents are immiscible in water and they enter the subsurface as a separate or nonaqueous phase. These immiscible fluids are generally referred to as non-aqueous phase liquids (NAPLs).

NAPLs are divided into two categories based on their density. If the NAPL is less dense than water, it is classified as an LNAPL or light non-aqueous phase liquid. In the Air Force, the majority of LNAPLs are petroleum hydrocarbons from gasoline and aviation fuel. On the other hand, if the NAPL is denser than water, it is called a DNAPL or dense non-aqueous phase liquid. The majority of the DNAPL contaminants at Air Force sites are from chlorinated solvents such as trichloroethylene (TCE) (Gorelick et. al., 1993).

LNAPLs and DNAPLs behave differently when spilled, and therefore different clean up techniques must be employed to ensure the clean up is effective. How each NAPL migrates through the soil is also dependent on how the contamination occurred, such as volume, area and duration of release, the soil media, and groundwater flow conditions (Knox and Sabatini, 1992).

When LNAPLs are spilled, the contaminant will migrate downward only if there is sufficient amount of the LNAPL available to fill the soil pore spaces to greater than residual saturation of the soil. Residual saturation is the point at which the LNAPL becomes discontinuous and immobilized by capillary forces. As more LNAPL fills the soil pore spaces the LNAPL travels downward through the pores of the soil until the capillary fringe of the water table is reached. The LNAPL will then begin to mound at the top of the capillary fringe, and "float" above the water table. The LNAPL initially spreads laterally initially due to gravitational forces, but as the pool of LNAPL builds, capillary forces control the spreading in the vadose zone (Knox and Sabatini, 1992, Testa, 1994). Since LNAPLs are found on top of the water table or in the vadose zone, they are

easier to detect than DNAPLs. Figure 1 is a conceptual representation of LNAPL groundwater contamination.

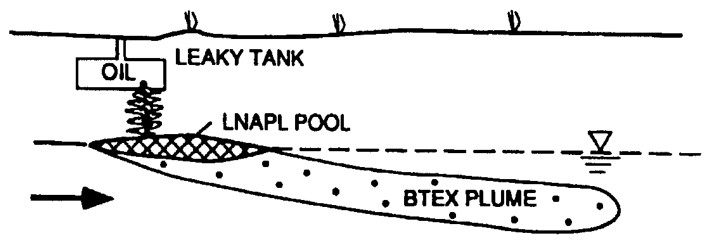
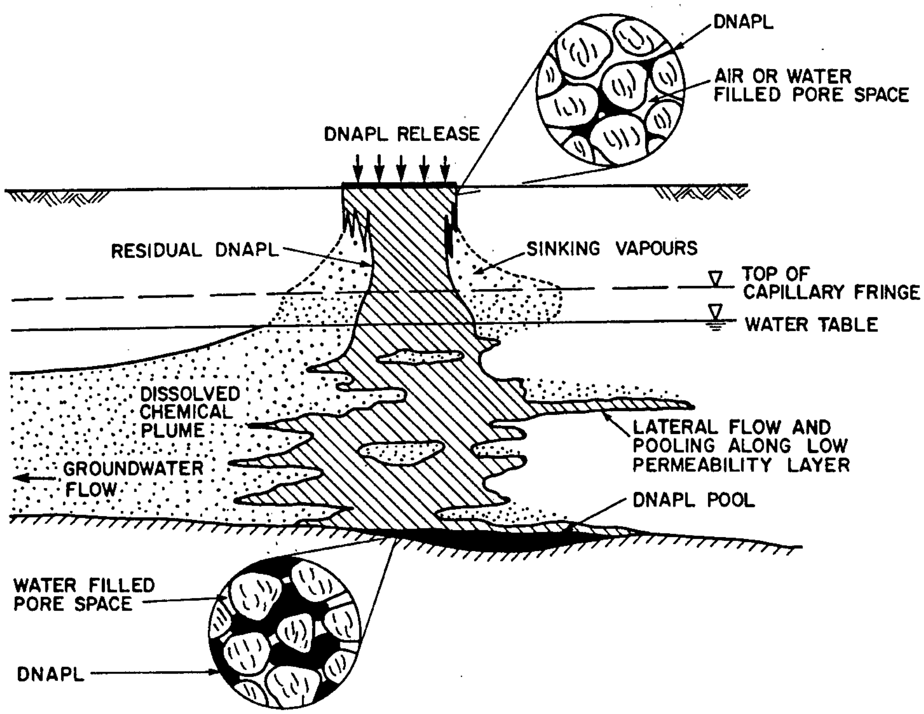


Figure 1. General groundwater contamination scenario associated with light nonaqueous phase liquids (LNAPLs) (Cherry and Pankow, 1996)

If a DNAPL is spilled, the fluid will, as with LNAPLs, move downward through the vadose zone (Cohen and Mercer, 1993). DNAPL chemicals are distributed in the vadose zone by volatilizing into soil gas, sorbing to soil grains, dissolving in groundwater, and remaining as a separate phase liquid (Cohen and Mercer, 1993). In the vadose zone, the DNAPL will behave just as an LNAPL, migrating downward until it reaches the capillary fringe. At the capillary fringe, the DNAPL begins to mound and head is built up. Ultimately, as head builds, the DNAPL will displace the water held by capillary forces. Unlike a LNAPL spreading above the water table, a DNAPL will continue to travel downward as a separate phase through the saturated zone until it encounters a significant permeability contrast (Cohen and Mercer, 1993). If the low permeability layer slopes in a direction that varies from the hydraulic gradient, the DNAPL will move in a direction different from the direction of groundwater flow. The

DNAPL density and viscosity, as well as the subsurface geology of the aquifer, control how the DNAPL is distributed in the subsurface. The rate at which the DNAPL sinks increases with increasing density and decreasing viscosity (Kueper and Frind, 1991). When the DNAPL penetrates the water table, it travels downward as distinct fingers rather than as a continuous front. Fingering is caused by heterogeneity in the soil. Soil with high permeability will permit a lot of liquid to enter, thus allowing larger fingers while low permeability soil permits only smaller fingers (Kueper and Frind, 1991). As fingering is a random phenomenon and the location of soil permeability contrasts is unknown, it is extremely difficult to predict the actual location of the DNAPL beneath the water table. Unstable flow can also occur when more dense fluid imbibes less dense fluid, or due to viscosity. Once the DNAPL reaches an aquitard or impermeable layer, the DNAPL will spread out laterally due to gravitational forces and due to viscous drag from the groundwater above (Knox and Sabatini, 1992). The DNAPL will tend to fill in lows of the impermeable layer. The DNAPL pool will collect in the lowest portion of the aquifer, and will reflect any unevenness of the surface it rests upon. Fractures in the "impermeable" layer allow the DNAPL to penetrate even deeper. DNAPL movement is also influenced by small pore openings such as may be found in clay strata. The DNAPL in the saturated zone acts as a mobile and permanent source for dissolved constituents entering the groundwater (Gorelick et.al., 1993). Figure 2 is a conceptual representation of a DNAPL contaminant scenario (Kueper and Frind, 1991).



General groundwater contamination scenario associated with dense, nonaqueous phase liquids.

Figure 2. General groundwater contamination scenario associated with dense nonaqueous phase liquids (DNAPLs) (Kueper and Frind, 1991)

As shown in figures 1 and 2, both DNAPLs and LNAPLs serve as the source for plumes of dissolved contaminant. Pump and treat is currently being used to remediate contaminated sites. This method has been shown to be unsuccessful at remediating an aquifer, though it is useful in containing the movement of contaminants (Mackay and Cherry, 1989). The Air Force is concerned over costs of long-term operation of pump and treat systems to control contaminant migration. A typical pump and treat system costs between $400 to $500 thousand per year to operate (Intera, 1997). Air Force installations' cleanup budgets are being increasingly used for the operations and maintenance of pump and treat systems, resulting in a lack of funds to support other

remediation activities. It is therefore critical from a budgetary viewpoint, that contaminant source areas be removed.

Technologies currently exist that can clean up LNAPLs that have reached the aquifer and both LNAPLs and DNAPLs in the vadose zone (Cherry and Pankow, 1996). However, since DNAPLs may have migrated beneath the water table, they are more difficult to remediate. Scientists and engineers are currently developing new technologies to deal effectively with DNAPLs that have migrated below the water table.

1.2 DNAPL Remediation Techniques

There are currently three strategies being investigated to remediate DNAPL contamination in aquifers. These are direct pumping, mass destruction, and enhanced mass removal of the NAPL.

As the name implies, direct pumping involves pumping a pool of DNAPL out of the subsurface using wells screened at the bottom of the pool. This technique has obvious difficulties that will be discussed in more detail in the following chapter. The major difficulty is the inability to locate substantial DNAPL pools in the subsurface. Even if a pool can be located, however, pumping can only remove a maximum of one-half or two-thirds of the DNAPL. The DNAPL not removed remains as a virtually permanent source for dissolved constituents (Cherry and Pankow, 1996).

The second strategy involves mass destruction. Mass destruction technologies are in situ techniques that destroy the DNAPL by chemical oxidation or microbial degradation. Chemical oxidation involves flushing an oxidizing agent through the

DNAPL to decompose the contaminant. Microbial degradation uses chemical additives to stimulate bacteria already in the soil to "eat" or degrade the contaminant in place.

The last strategy being investigated involves mass removal technologies. Mass removal technologies use a basic pump and treat system that is enhanced by one of several different means to improve the efficiency of the DNAPL removal. These enhancement technologies have the potential to greatly reduce the time required for removal of the contaminant from the subsurface. Enhanced removal can be accomplished thermodynamically, through air sparging, or chemically. Thermodynamic enhancement involves injecting hot fluid (liquid or gas) or directly heating the contaminated zone. For example, steam stripping has been used to volatilize DNAPL and remove it from the subsurface as a gas phase. This is possible because the chlorinated solvents typically have boiling points lower than water (Cherry and Pankow, 1996).

Air sparging injects air into the saturated zone below or near a contaminated area. As the air rises, dissolved and NAPL phase contaminants in contact with the air partition into the gas phase (McCray and Falta, 1997).

Chemical enhancement of solubility may involve the injection of a surfactant or cosolvent. The injection of a chemical can increase the contaminant's solubility in the pumped groundwater or cause the bulk DNAPL to move as a separate phase depending on the amount of chemical added to the aquifer. Surfactants and cosolvents increase the solubility of the NAPL in the liquid phase (Dawson and Roberts, 1997). While typically surfactants and cosolvents are used to increase solubility, the DNAPL can also be mobilized by adding larger quantities of surfactants or cosolvents to the contaminated area (Lowe, 1996). Mobilization has generally been avoided because of the potential risk

of downward migration of DNAPLs. However, mobilization has been used in density modified displacement (DMD) techniques. Density modified displacement involves adding chemical (typically as alcohol) that partitions into the DNAPL, resulting in a decrease in the DNAPL's density. If the DNAPL's density is lowered sufficiently, when it is mobilized it behaves as a LNAPL and moves upward, where it can be easily more recovered. DMD has utility when the DNAPL has a relatively low density and solubility, such as coal oil (Lowe, 1996). This is because a lower density DNAPL requires less alcohol to be added to transform it into a LNAPL. A DNAPL with higher density requires much more alcohol to be added. Of course, high solubility DNAPLs may be removed by solubilization instead of mobilization.

1.3 Scope and Limitation

Chemically enhanced treatment using surfactant and cosolvent flushing has great potential to remediate DNAPL below the water table. Both surfactant and cosolvent technologies were tested in field experiments at Hill AFB with promising results. As surfactant flushing has been studied in other field experiments and applied at several real world sites, and cost effectiveness studies of surfactant flushing have already been accomplished (e.g. Harwell et.al., 1995), this thesis will focus on cosolvent flushing, which has not been studied nearly as extensively. In this work, a cost and effectiveness evaluation of the technology will be based on the cosolvency theory developed by Dr Rao (Ward et.al., 1997). Based on this theory, a cost-performance model may be developed and used to compare the cost effectiveness and efficiencies of cosolvent flushing to other remediation techniques such as surfactant flushing.

Chapter 2

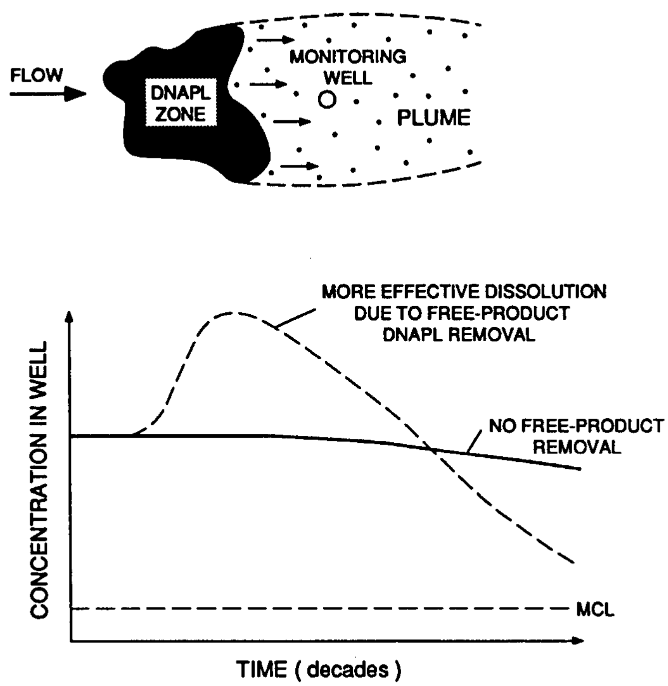
Literature Review

2.1 Evaluating Competing Technologies

As discussed in Chapter 1 there are currently three strategies that are available to remediate DNAPL in the saturated zone. These are direct pumping, mass destruction, and mass removal of the NAPL.

2.1.1 Direct Pumping.

Direct pumping has been used in the past to clean up DNAPLs (Cherry and Pankow, 1996). This technology is used when large pools of DNAPL are located. Some pools are large enough to allow pumping of free-product DNAPL from the wells. Using two pumps enhances the DNAPL removal of direct pumping. One pump is located in the DNAPL pool, and the other pump is located in the groundwater above the pool (Cherry and Pankow, 1996). The flow of water across the pool increases the DNAPL flow toward the DNAPL pumping well. DNAPL free-product removal is limited to a maximum of one-half to two-thirds of the total DNAPL in the aquifer (Cherry and Pankow, 1996). The remaining DNAPL in the aquifer is trapped as ganglia in the soil pores and is difficult to be removed by a pumping well. The free product removal limitations are seen in figure 3 on the next page. The entrapped ganglia act as a long-term source of contamination. The contaminant flux into the groundwater declines over time as the ganglia dissolve. Although remediation of ganglia is faster than remediating a pool of contaminant, it still takes approximately 30-100 years for the ganglia source area to disappear (Falta et.al., 1996).



MCL = maximum concentration level for drinking water use.

Schematic illustration of the effect of free-phase DNAPL removal on the downgradient plume concentration. After free-phase DNAPL is removed from pools, dissolution of the remaining DNAPL (residual) produces a temporarily greater contaminant flux.

Figure 3. DNAPL characteristic curve illustrating limitations of direct pumping remediation method. (Cherry and Pankow, 1996)

Since direct pumping is not effective for remediating DNAPL using current technologies, other remediation techniques are being investigated. Work is focusing on two remediation strategies. These are (1) in situ destruction of DNAPL or (2) DNAPL solubilization/mobilization and removal. These technologies are discussed in the following sections.

2.1.2 Mass Destruction Techniques.

In situ mass destruction attempts to remediate DNAPL by destroying it in place. Mass destruction of the DNAPL can be accomplished chemically or biologically. Chemical mass destruction techniques involve the use of an oxidizing agent such as

hydrogen peroxide to chemically break the bonds of organic contaminants. Using Fenton's reaction, hydrogen peroxide and iron are used to oxidize DNAPLs such as TCE, into carbon dioxide, water, hydrogen, and chloride ions. Destruction efficiencies as high as 94% have been claimed (Geocleanse, 1998). Although early results are promising, (Cherry and Pankow, 1996), this technology cannot be used when the pH of the groundwater is greater than 8.0, the contaminant is strongly sorbed to a soil with high organic carbon content, or the groundwater hardness exceeds 400 parts per million (Geocleanse, 1998). The method also requires careful control of the chemical reaction since considerable heat is generated (Haselow, 1996). Controlling heat generation is essential to keep volatile organic compounds such as TCE from being transferred to the gaseous phase. Also, if the hydraulics of the chemical spike are not properly controlled, contaminants could be pushed to clean zones by the injected water (Haselow, 1996). Other concerns relating to the use of oxidants in the subsurface relate to reaction by-products. For example, chloroform may be created as an intermediate product during oxidation of TCE (Haselow, 1996).

The second mass destruction technique is through bioremediation. In situ bioremediation may involve introducing cultured or genetically-engineered bacteria into a contaminated zone (bioaugmentation), or stimulating indigenous bacteria with nutrients (biostimulation). The bacteria then break down the organic chemicals metabolically. Bioremediation however, has achieved limited success in remediating DNAPLs since the high aqueous contaminant concentrations near a DNAPL zone are typically toxic to bacteria. This severely limits microbiological remediation as an effective means of restoring DNAPL source areas (Cherry and Pankow, 1996). Microbiological methods are

best used for assisting in source-zone restoration when applied at a later stage, after other enhancement methods have lowered the concentrations below microbial toxicity limits. Bioremediation is most effective for the degradation of dissolved contaminants (Haselow, 1996).

2.1.3 Enhanced Removal Techniques.

Beneath the water table, basic pump and treat systems have been used in the past in attempts to remove DNAPLs. The clean up rates using this technique are extremely slow, usually between 10-30 years to achieve clean up (McCray and Falta, 1996). Because of the low aqueous solubility of the DNAPLs, the projected clean up time for some remediation projects can even extend to one hundred years or more (Falta et. al., 1996). Particularly in the later stages of the site clean up, the basic pump and treat system becomes more difficult since the dissolution rates become mass transfer limited (Ward et. al., 1997). At these later stages, the recovery rates are proportional to the aqueous phase diffusivities of the contaminants, which are usually small (Ward et. al., 1997). Since basic pump and treat techniques are inefficient and costly, scientists are seeking ways to enhance this removal technique. Two strategies are being investigated to enhance DNAPL removal: thermodynamic and chemical enhancement. Also, air sparging is a technique that has the potential to enhance the removal of DNAPLs, and it will also be discussed in this review.

2.1.3.1 Thermodynamic Enhancement.

Thermodynamic enhancement can be accomplished by adding heat energy to vaporize the contaminant. It does not involve introducing a chemical into the soil. Introducing heat energy into the subsurface increases the temperature of the contaminant.

Thermodynamic enhancement can be accomplished by electrical heating, radio frequency heating, and hot air, hot water or steam injection. Electrical heating and radio frequency heating applies energy directly to the subsurface without the injection of any substance. Electrical heating is accomplished by inserting electrodes into the ground. An electrical current is applied through the electrodes using water as a conductor. The resistance to the flow of current in the soil causes heat to be generated. As the soil is heated, the soil moisture evaporates and the contaminants volatilize (Ward et. al., 1997). Electrical heating has only been performed in pilot-scale tests. Since there is no full-scale experience with electrical heating it is unknown if this technology will work in the field (Nyer and Kidd, 1996). The technology also requires large energy inputs to heat the soil. The energy required to raise the temperature of a soil high enough to remediate a DNAPL is very high. For example, to remediate a sandy clay to 100 degrees Celsius and vaporize all of the water in the area of interest requires an energy input, of 180 to 200 kWH, costing between $18 to $20 per cubic yard (Falta et. al., 1996). "Although the technology concept is sound," large energy requirements make this technology impractical (Falta et.al., 1996).

Radio frequency heating uses excitor electrodes to heat the soil. A radio frequency transmitter is connected to the electrodes. Heat is generated by the resistance

of the soil to electrons moving through it, similar to electrical heating. Also, magnetic distortion of the molecular structure of water causes dielectric heat to be generated. Heating of the soil often occurs preferentially in zones or pathways that have the highest electrical conductivity or radio frequency absorptivity (Ward et. al., 1997). There are several other disadvantages of radio frequency heating including high equipment costs, intensive operator control required, and the possibility that the high temperatures that can be created by the method may sterilize the soil and inhibit future biodegradation potential. In addition to this, the technology has limited field application (Nyer and Kidd, 1996)

The third thermodynamic technique is hot gas injection. This technique involves injecting air at high temperatures to increase volatile organic compound's vapor pressures and desorption of contaminants from soil surfaces. Hot gas injection has been used in the unsaturated zone. However, below the water table its application is more difficult since the low specific heat of air does not make it a good choice as a heat injection fluid. The air would have to be heated to a temperature exceeding 2200 degrees Celsius (Ward et.al., 1997) to have the same energy injection rate of steam since the heat capacity of air is about 1kJ/kg-C and the enthalpy of vaporization of water is over 2200 kJ/kg. Therefore, heating the subsurface with steam is a more efficient process.

Another thermodynamic technique involving the same principles as hot gas injection is hot water injection. Hot water injection also accelerates the clean up of contaminants by decreasing adsorption, interfacial tension, density, and increasing solubility. Unlike steam enhanced extraction which relies on a steam front to displace contaminant, hot water injection uses a hot water front to mobilize the NAPL. This remediation technique is accomplished by injecting hot water below the contaminated soil

zone resulting in heating of the soil and pore fluids. The DNAPL is mobilized upward providing that it becomes less dense than water under the applied temperature. As the DNAPL migrates upward, a concentrated NAPL mound may form ahead of the propagating hot-water front. Early laboratory results have demonstrated that 84% to 94% reduction of hydrocarbon is achievable under homogenous soil conditions (Grubb and Sitar, 1994). This technique is limited to areas of high permeability, where the water can reach all of the contaminant easily (Falta et. al., 1996).

Steam injection and fluid extraction is similar to hot air and water injection. This technique overcomes the problems of the extremely large energy requirements and phase transport problems of hot gas and water injection. Steam injection achieves greater NAPL recoveries than hot water floods and requires less liquid to be injected (Hunt et. al, 1988). This technique injects saturated steam into a cool porous media through a series of wells (Nyer and Kidd, 1996). The steam then condenses and heats the soil and contaminants. Through continuous steam injection, three temperature zones in the soil will develop. The first zone is the isothermal steam zone where the steam is first introduced into the soil. The variable temperature zone is the location of the temperature gradient that ranges from the temperature at which the steam is introduced to the temperature of the soil media. The last zone is also an isothermal zone that remains at the original temperature of the soil (Ward et. al., 1997). Displacement of the contaminant is accomplished by moving the steam condensation front using high steam pressure gradients (Ward et. al., 1997). Condensation of the injected steam occurs between the steam zone and the variable temperature zone. Extraction wells are used to withdraw the water and volatilized contaminants from the soil (Nyers and Kidd, 1996).

The steam heats and displaces the water from high to medium permeability zones. Low permeability zones can be heated by conduction when surrounded by steam injection regions (Ward et. al., 1997). Steam injection increases the rate of contaminant recovery, since it effectively heats the soil (Ward et. al., 1997). The injection of steam dilutes and displaces nonvolatile contaminants from regions below the water table. This removes water from the contaminant-laden strata, providing additional area for the steam to contact the contaminant again. This technology allows for greater gas-DNAPL contact and nonvolatile solute removal thereby, dramatically decreasing the remediation time (Falta et. al., 1996). Steam flushing has previously been used in the petroleum industry to enhance the recovery of oil. The application of the technology is limited by the heterogeneity of soil and impermeable layers that impact the pathways where the steam travels (Nyers and Kidd, 1996). Also, large equipment costs are incurred because of the need for steam generation equipment. Another major disadvantage of this technology is the potential for downward migration of the DNAPL that would make remediation even more difficult (Falta et. al., 1996). Fortunately, heating the DNAPL has the effect of decreasing the potential for downward migration, so it is unlikely that the DNAPL will mobilize downward using this technology (Heron et. al., 1998).

2.1.3.2 Air Sparging

Another example of an enhanced removal technology is air sparging. Air sparging remediation involves injecting air into the saturated zone below or near a contaminant source. As the air rises to the surface, NAPLs volatilize into the gas phase and are removed from the aquifer. Air sparging is usually used in concert with soil-vapor

extraction to remove contaminant from the vadose and saturated zones simultaneously (McCray and Falta, 1996). Air sparging has been used successfully on LNAPL because it can directly target the capillary fringe where LNAPLs concentrate. Air sparging also stimulates biodegradation. If the biodegradation is significant enough, soil-vapor extraction may not be necessary, thus avoiding the costs of above ground contaminant treatment (Falta et. al., 1996). Air sparging is generally used when contaminants are in a shallow aquifer or the capillary fringe. Air sparging utilizes relatively cheap equipment since the motors used to run the system require low horsepower, and air rather than water is used as the transport medium. Spacing between each of the sparge wells must be close, however, in order to achieve maximum removal effectiveness. This often requires more wells than other remediation techniques, though fortunately, air injection points are considerably less expensive to install than groundwater recovery wells (Falta et. al., 1996).

There are several limitations to air sparging however. Sites where DNAPLs are present in pools on top of impermeable layers may not be effectively remediated since it is difficult to create direct air contact. Sites with widely dispersed areas of pollution are difficult to remediate using air sparging due to the limited effective radius of the air being injected. Stratified soil layers also limit the technology's effectiveness. These layers create preferential pathways making it difficult to expose all of the contaminated areas to the gas. Finally, air sparging is not effective in sites with low permeability, sites that are highly fractured or sites having contaminants that are semi volatile or nonvolatile.

2.1.3.3 Chemical Enhancement.

Chemical enhancement will be defined as the use of water with chemical amendments to increase contaminant removal. Chemical enhancement can be used to mobilize the bulk DNAPL or increase the DNAPL's solubility, depending on the characteristics and quantity of the chemical additive.

Surfactants and cosolvents are the two main classes of amendments that are being used to either mobilize or solubilize DNAPLs. We will begin with a discussion of surfactants.

Surfactants, or surface-active-agents, have a characteristic structure. The molecules have a hydrophobic (water fearing) structural group and a hydrophilic (water loving) structural group. The hydrophobic portion of the surfactant is typically a long, nonpolar hydrocarbon chain, while the polar hydrophilic "head" often includes anions or cations such as sodium, chloride, or bromide. Because of these structures, surfactants accumulate at interfaces, particularly the NAPL-water interface. Surfactants may be classified by charge (cationic, anionic, nonionic or twitterionic), source (biosurfactant or synthetic surfactant) or regulatory status (indirect food additive, acceptable for use in pesticide formulations, biodegradable in waste treatment processes, detergents, etc.) (Falta et. al., 1996).

As noted earlier, surfactants can be used to either mobilize or increase the solubility of the NAPL. Let us first examine how surfactant flooding is used to enhance the solubilization of the NAPL. When surfactant-water solution is pumped through NAPL-contaminated zone, the solubility of the NAPL the water-surfactant solution is much greater than the NAPL solubility in water alone (discussed below). Residual and

pooled NAPL dissolves away in fewer pore volumes than would be required by pumping water alone. During surfactant flooding, surfactant monomers are added to the contaminated aquifer. The hydrophilic group of the surfactant provides the surfactant with a high solubility in water, while the hydrophobic portion resides in the hydrophobic phase such as a LNAPL or DNAPL. Figure 5 shows surfactant monomers accumulating at the NAPL-water interface, with the hydrophobic end of the surfactant in the NAPL phase and the hydrophilic end in the water phase. Surfactant monomers also accumulate at the water-air and water-solid interfaces (Lowe, 1996). Once a sufficient concentration of surfactant monomers has been added to the water, aggregates of surfactants will form called micelles (Figure 4). The threshold concentration at which micelles begin to form is termed the critical micelle concentration (CMC). Figure 5 shows the threshold concentration at which micelles begin to form. As the figure shows, above the CMC, an increase in surfactant concentration does not lead to an increase in monomers, since the additional surfactant molecules aggregate as micelles. As shown in figure 4, micelles form with the hydrophillic ends facing out into the water, and the hydrophobic ends of the surfactant molecules facing inward, forming a hydrophobic phase.

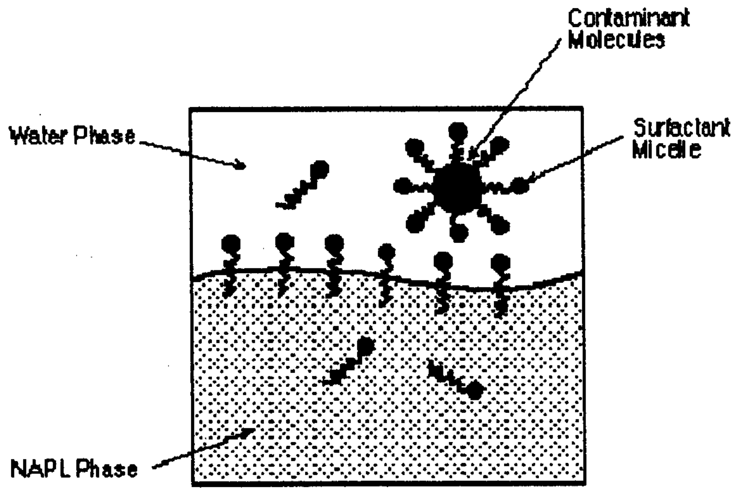


Figure 4. Illustration of micelle (Lowe, 1996).

When surfactant is present as monomers, the contaminant's solubility is somewhat increased. However, once the surfactant concentrations exceed the critical micelle concentration, the solubility of the contaminant increases significantly. Contaminant molecules partition into the hydrophobic phase found in the center of the micelle, thus increasing the total solubility of the contaminant in the water-surfactant phase in a process called micellar solubilization (Lowe, 1996). Increasing the total aqueous solubility of the NAPL will accelerate the dissolution of the NAPL (Lowe, 1996).

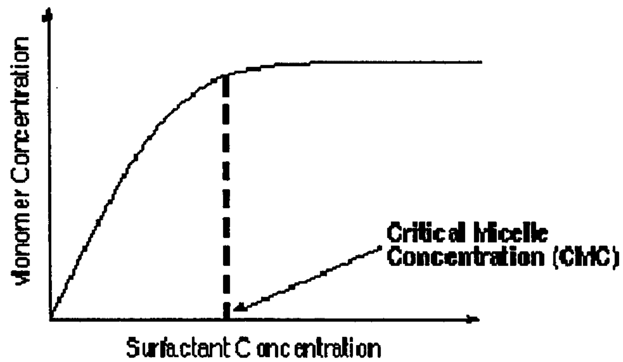


Figure 4-3
Formation of micelles at critical micelle concentration (CMC)

Figure 5. Formation of micelles at critical micelle concentration (Lowe, 1996).

Micelles provide an excellent sink for organic contaminants (Falta et. al., 1996). The greater the surfactant concentration, the larger the solubility enhancement anticipated (Falta et. al., 1996). Note, though, that surfactants are extremely sensitive to temperature. Below a certain temperature known as the Krafft point, micelles will not form and therefore the surfactant solution will have no potential to increase the solubility by micellar solubilization (Lowe, 1996). The Krafft point is the temperature at which the aqueous solubility of ionic surfactant equals the CMC. Nonionic surfactants are also affected by temperature. They are subject to coacervation at high temperatures. This is when a separate surfactant rich phase forms. This precipitation of the nonionic surfactant is undesirable because it lowers the amount of surfactant available for micellar solubilization (Lowe, 1996).

The second way to use surfactants is to mobilize the NAPL. This is accomplished by using the surfactant to reduce the NAPL-water interfacial tension sufficiently to overcome the capillary forces that hold the NAPL in place as either residual NAPL or

pooled NAPL. If the interfacial tension can be lowered sufficiently, physical mobilization of NAPL can occur. The ability of the surfactant to reduce the interfacial tension required to mobilize residual NAPL can be best characterized by the capillary number which is the ratio of viscous to interfacial forces and is defined by the following equation: (Lowe, 1996)

$$Nc = k*g*J*\rho/\sigma \tag{1}$$

Where

Nc = capillary number [-]

ρ = density of water $[M/L^3]$

g = acceleration due to gravity $[L/T^2]$

J = hydraulic gradient [-]

σ = NAPL-water interfacial tension $[M/T^2]$

k = permeability $[L^2]$

Mobilization occurs when viscous forces are greater than interfacial forces (that is Nc is large). Thus, an increase in hydraulic gradient or a reduction in the interfacial tension favors mobilization.

The reduction of the NAPL-water interfacial tension that will occur upon exposure to surfactants depends strongly on the particular NAPL-surfactant combination. Only certain surfactants are capable of lowering interfacial tension by the amount necessary to mobilize significant quantities of residual NAPL (Lowe, 1996). Mobilization in a surfactant flood occurs when enough surfactant is added to form a separate middle phase microemulsion. This separate phase is a microemulsion of micelles and structured aggregates of micelles. The formation of this third phase (water

and NAPL being the other two phases) is associated with ultra-low interfacial tensions between the NAPL and water phases. The micro emulsion has a density between the water and NAPL phases (Lowe, 1996).

In a typical mobilization flood, a certain degree of NAPL solubilization will also occur. The degree of solubilization can be manipulated to a desired level by selecting different surfactants or by using cosolvents.

Several problems have been noted with surfactant flooding. The first is surfactant sorption. The adsorption of surfactants to soil particles can lower the concentration of available surfactant in the aqueous phase. If the degree of adsorption is great, surfactant concentrations could drop below the CMC, leaving the surfactant largely ineffective. Surfactant partitioning into the NAPL phase must also be considered. Significant partitioning will also cause a reduction in the concentration of surfactant in the aqueous phase, so that more surfactant is needed to achieve the CMC (Lowe, 1996). Surfactants also may biodegrade. While the surfactant flooding is taking place, degradation of the surfactant will decrease the amount available for NAPL removal. Of course, once the remediation is complete, degradation of the surfactant is desirable. Note though that at high concentrations surfactants can kill microorganisms, preventing microbial degradation. In addition, availability of oxygen and other electron acceptors may limit biodegradation (Lowe, 1996). Regulatory concerns regarding surfactant fate and toxicity also limit its use for remediation.

Downward migration of the NAPL is a possible consequence of surfactant flooding. As a result, mobility control is essential to ensure that the injected surfactants contact the contaminated regions and do not mobilize the DNAPL into previously

uncontaminated areas (Falta et. al., 1996). Technology to control mobilization of the DNAPL is currently being explored. Unfortunately, the mobility control technologies have not been fully investigated and field tested. Therefore the use of surfactant flooding to mobilize the NAPL has yet to be demonstrated at full scale.

2.2 Cosolvent Remediation

2.2.1 Overview

The last method of chemical enhancement that will be considered is cosolvent flooding. Cosolvent flooding involves the injection of a water miscible solvent such as an alcohol or propylene glycol upstream of the contaminated zone. The contaminant-solvent mixture is then extracted downstream and treated above ground to recover the solvent (Rao et. al., 1994). The miscible solvent or alcohol reduces the interfacial tension between the aqueous and DNAPL phases. Alcohol can then solubilize the DNAPL or mobilize it depending on the alcohol selected, contaminant present and the concentration used. Low concentrations of alcohol have been shown to increase the aqueous solubility of organic contaminants. In a low-concentration, alcohol flood (usually 1-5%), where the system remains a two-phase (NAPL-water) system, many pore volumes of solution need to be flushed through the NAPL zone to achieve significant removal without mobilization of the NAPL (Lowe, 1996). If the alcohol concentration is relatively low, and an alcohol is used that preferentially partitions into the DNAPL phase, the DNAPL phase will swell, while the interfacial tension between the water-DNAPL phase will decrease, and the solubility of the NAPL will increase. The DNAPL dissolves into the alcohol-water mixture and maintains two phases, since the concentration of alcohol is not great enough to create a one-phase system. The goal of solubilization is to dissolve the NAPL without

mobilizing it. If there is a relatively high concentration of alcohol, the DNAPL-water interfacial tension would become very small so that essentially there would be only one fluid present in the aquifer. This results in mobilization of the contaminant. When high concentrations of alcohol are used the term alcohol flooding is typically used. The term cosolvent flooding is used when alcohol concentrations are relatively low. The goal of mobilization is to remove the NAPL as rapidly as possible. Brandes and Farley (1993) found that NAPL mobilization was the main mode of NAPL recovery in systems where the cosolvent preferentially partitions into the NAPL phase, known as a type II (+) system. Similarly they found that NAPL dissolution was the main mode of NAPL recovery in systems where the cosolvent preferentially partitions into the aqueous phase, known as a type II (-) system. It is not clear which removal method is most desirable for field applications (Falta et. al, 1996). The mobilization of the DNAPL is more efficient since it requires less solvent. However the potential for downward migration also exists. The potential for downward migration depends on the density difference between the DNAPL and the aqueous phase, the flow conditions and the permeability of the soil. This greatly depends on the cosolvent chosen (Falta et. al, 1996). Studies are currently underway to swell the DNAPL so as to decrease its density, ultimately turning the DNAPL into a LNAPL before mobilizing it. This technique, also known as density modified displacment, has yet to be tested in the field (Falta et al, 1996).

There are several limitations to this technology. Since cosolvent technology is still emerging its limitations are not well known. Some cosolvents are flammable and moderately toxic and may not be approved for application as a clean up technique. This limitation will be discussed further in the legal issue section of the literature review. Also

early studies indicate that in order for this remediation technique to be viable the cosolvent must be recycled and reinjected back into the aquifer (Lowe, 1996).

2.2.2 Theory of Cosolvent Technology

The theory of using cosolvents to remediate DNAPL contaminated sites originated from the petroleum industry. In the petroleum industry alcohol flooding was proposed as a method of enhanced oil recovery in the early 1960's. Early studies demonstrated alcohol's ability to completely remove trapped oil from soil cores. The technology however was never used due to the expense of alcohol relative to the increase in amount of oil recovered. As DNAPL remediation in groundwater became an increasingly difficult problem, a number of scientists began to investigate the feasibility of using cosolvent flooding to remediate DNAPL contamination (Falta, 1998).

It was found that the addition of alcohol led to an increase in solubility of the nonpolar organic contaminants. Early studies established a log-linear relationship between the solubility of hydrophobic organic compounds when a cosolvent is added (Rao et al, 1994).

The theory of using cosolvents to cleanup soils began with Yalkowsky and Roseman who established the following relationship (Ward et. al., 1997):

$$\text{Log}(S_m) = \text{Log}(S_w) + \beta^* \sigma^* f_c \qquad (2)$$

Where

S_m = Solublity of nonpolar organic solute in solvent (alcohol-water) mixture

S_w = Solubility of nonpolar organic solute in water

β = Empirical coefficient that accounts for water-cosolvent interactions

σ = Cosolvency power

f_c = Fraction of cosolvent

Yalkowsky and Roseman proved that by adding a solvent, such as alcohol, the solubility of a hydrophobic contaminant increased in a log linear relationship with fraction of cosolvent (fc). This relationship is shown in figure 6.

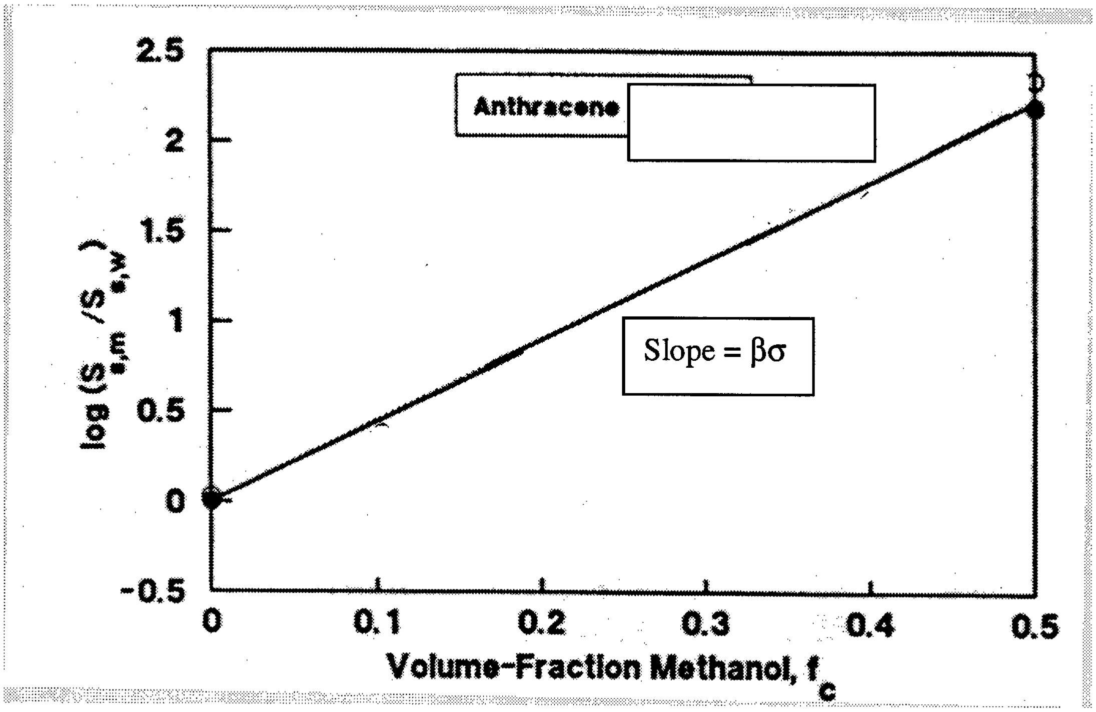


Figure 6. Log-linear relationship of NAPLs and cosolvents (Yalkowsky, 1990)

The figure shows the effects of the alcohol methanol on anthracene solubility. The cosolvency power (σ) is a critical parameter. Cosolvency power is a function of the solute molecular surface area and the interfacial free energy of the cosolvent. It can be derived using thermodynamic principles (Ward et. al, 1997). The solubility of a DNAPL contaminant will increase with decreasing polarity of the alcohol. For this reason, contaminant hydrophobicity indexes can be used to estimate the cosolvency power of an

alcohol for a particular contaminant. Using the octanol-water partition coefficient as the hydrophobicity index, the following relationship was developed (Ward et. al., 1997).

$$\sigma = A * \log(K_{ow}) + B \qquad (3)$$

Where

A, B = Empirical constants unique to each cosolvent

K_{ow} = Octanol-water partitioning coefficient of the DNAPL

Given the solubility relationship, it is possible to calculate how long it will take to cleanup a contaminated area based on the percentage of cosolvent added. First, we must calculate the number of moles of contaminant in the source area. This is determined by the following equation (Enfield, 1998):

$$\text{Moles Contaminant} = (Sat * Mole_f * \theta * Volume * \rho)/MW_n \qquad (4)$$

Where

Sat = Saturation of the NAPL [0 – 1], which indicates what fraction of the pore space is occupied by NAPL

$Mole_f$ = Mole fraction of contaminant of interest in relation to the total NAPL present [0-1]

θ = Porosity of the aquifer

Volume = Volume of contaminated zone [L^3]

ρ = Density of the DNAPL [M/L^3]

MW_n = Molecular weight of DNAPL [M/mol]

Next, we must determine the rate at which contaminant can be removed (moles removed per time). This is determined through a series of calculations developed based on the

solubility relationship. Knowing the solubility of the contaminant in the alcohol-water mixture, we multiply the pumping rate to determine the rate at which the mass can be removed from the aquifer. This equation only takes into account effects from a solubilization flood. It does not consider mobilization of the alcohol, which would decrease the amount of time needed to clean up a source area.

$$\text{Rate Mass Removed} = (S_w * \text{Theta}_w + S_c * \text{Theta}_c) * Q \quad (5)$$

$$\text{Theta}_w = 1 - \text{Theta}_c \quad (6)$$

$$\text{Theta}_c = \text{Percent}_a / 100 \quad (7)$$

$$S_c = (10^{\sigma}) * S_w \quad (8)$$

Where

S_w = Water solubility of contaminant [mol/L^3]

Theta_c = Fraction of cosolvent mixture that is alcohol (unitless)

Theta_w = Fraction of cosolvent mixture that is water (unitless)

S_c = Cosolvent solubility of contaminant [mol/L^3]

σ = Cosolvency power of the alcohol for the contaminant

Percent_a = Percentage of alcohol in cosolvent mixture

Q = Pumping rate [L^3/T]

Now, the time needed to remove the contaminants can be calculated using the equation below.

$$\text{Time} = (\text{Moles Contaminant})/(\text{Rate Mass Removed}) \quad (9)$$

Where

Moles Contaminant = Amount of contaminant present (equation 4) [mol]

Rate Mass Removed = Rate contaminant is removed (equation 5) [mol/T]

This approach assumes equilibrium. The equilibrium assumption can underestimate the length of time, volume of water, and cost required to decontaminate an aquifer (Powers et al., 1991). Since this thesis is meant to develop a rough cost estimate for using cosolvents to remediate a contaminated area, nonequilibrium effects are not taken into account. However, the reader should keep in mind that the equilibrium assumption, which is not conservative, is being used.

2.2.3 Determining Type and Concentration of Alcohol

As stated earlier, the percentage of alcohol injected into the aquifer determines whether solubilization or mobilization of the DNAPL will occur. A ternary phase diagram, similar to the one in figure 7, is used to illustrate the phase behavior of NAPL-water-alcohol systems. Ternary phase diagrams consist of tie lines and an independent miscibility envelope. In figure 7, each location inside the triangle corresponds to a specific water-ethanol-PCE mixture.

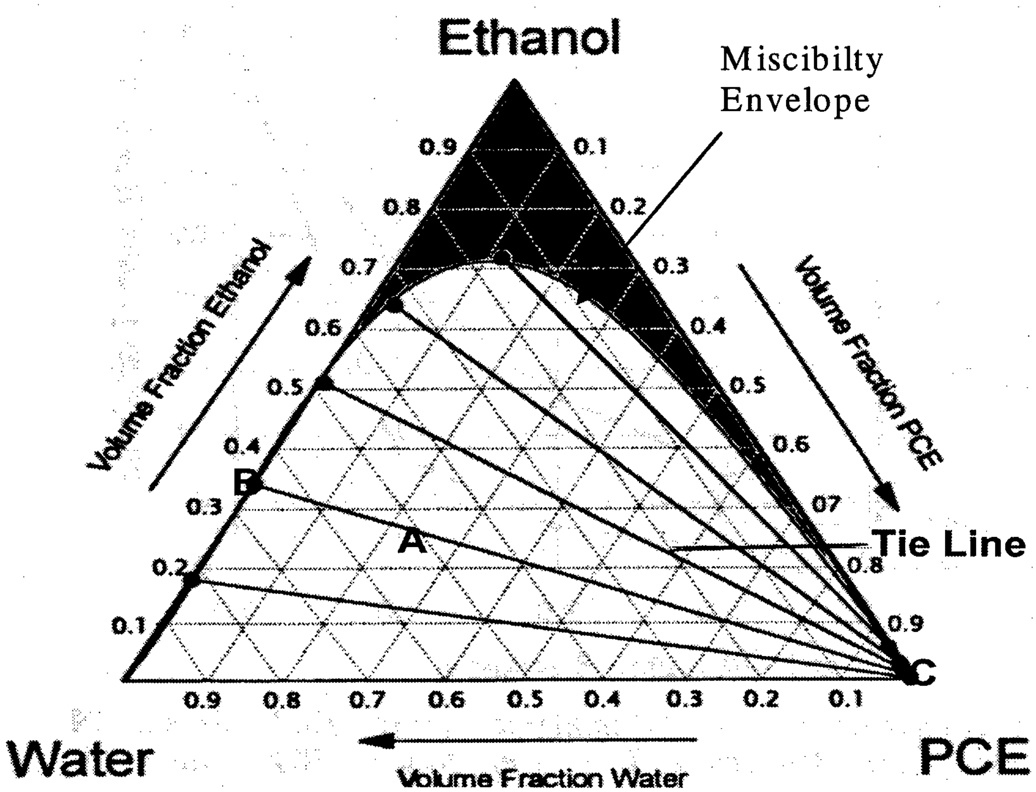


Figure 7. Ternary diagram of water, PCE, and ethanol (Lunn and Kueper, 1997).

In the area above the mound or miscibility envelope (colored in black above), all three phases of liquid are completely miscible. In this region, all of the components in the phase diagram will exist in a single phase and mobilization of the contaminant will occur. Below the envelope, a two-phase system exists with alcohol partitioning into both the water and NAPL phases. In order to determine the composition of the aqueous phase and NAPL phase, tie lines are drawn. Tie lines reflect equal partitioning of the alcohol between the aqueous and NAPL phases. For example, point A reflects an initial mixture of 25% PCE, 25% ethanol, and 50% water. This point in the ternary diagram corresponds

to a two-phase solution since it is below the miscibility envelope. The composition of each of the phases is determined from the endpoints of the specific tie line. The aqueous phase is approximately 35% ethanol, and 65% water (point B), while the NAPL-phase is 97% NAPL and 3% alcohol (point C). The left endpoint, point B defines the aqueous phase while the right endpoint, point C, indicates NAPL phase compositions. When the lines of the phase diagram slope toward the DNAPL, (i.e. as in figure 7) they have a negative slope. It shows that the alcohol has a strong preference for the aqueous phase (Lunn and Kueper, 1997). This is known as type II (-) behavior, and is depicted in the ternary curve above. This indicates that NAPL dissolution into the aqueous phase is the most efficient method to recover the NAPL. Some alcohols have a positively sloped tie line, and these are known as type II (+) system. This indicates that the alcohol would prefer to partition into the NAPL phase relative to the aqueous phase, so NAPL mobilization may be the most efficient method to recover the NAPL.

Before the ternary diagram can be used, the cosolvent must be chosen. Choosing the alcohol that will most efficiently remove the DNAPL is an extremely critical step. It is recommended that laboratory studies using the specific soil and contaminants be completed (Lowe, 1996). Currently, there is no widely accepted guide available to choose an appropriate cosolvent. However, Yalkowsky et. al. (1996) performed experiments to determine which alcohol-DNAPL characteristics could be used to predict the most effective cosolvent or alcohol in remediating DNAPL contaminants. His study suggests that the use of the interfacial tension between the NAPL and alcohol, and the solubility of the alcohol into the DNAPL provide the best indicators of how the cosolvent will perform. As noted earlier, the ability of the NAPL to solubilize into aqueous

solution will be improved when alcohol is added. If the interfacial tension and solubility of the NAPL are low, the cosolvency power, σ, of the alcohol for the DNAPL will be higher. The higher the cosolvency power of an alcohol, the faster the alcohol will be able to solubilize the NAPL into the aqueous phase. Alcohols with higher cosolvency power also require less alcohol to solubilize a DNAPL than alcohols with a lower cosolvency power. Previous studies mainly have looked at five alcohols, for use as cosolvents: methanol, ethanol, 1-propanol, 2-propanol, and tert-butyl alcohol (Lowe, 1996). This thesis will be limited to these five alcohols. The cosolvency power constants identified by Rao, as well as other properties for these five alcohols, are listed in Table 1.

Methanol or wood alcohol is a clear colorless liquid obtained from the distillation of wood. It is a common industrial solvent found in products such as paint removers, varnishes etc. Methanol itself is not toxic, however two metabolites, formaldehyde and formic acid, are highly toxic (Viccellio, 1993). Ethanol is also a clear, colorless liquid. It is a common solvent in many household cleaners, toiletries, and alcoholic beverages. It can be lethal to humans in large concentrations (Viccellio, 1993).

1-propanol also known as n-propyl alcohol is commonly used in the paint industry as a thinner. It is often added to lacquers and paints to improve their viscosity and flow characteristics. N-propyl alcohol is also used in the printing industry to keep ink level and flowing. It is a clear, low odor liquid. This alcohol is very flammable and has exploded when stored in sealed containers. Although not fatally toxic to humans in small concentrations, n-propyl alcohol should not be consumed. There are currently no medical conditions identified that are aggravated by consumption of the alcohol.

2-propanol or isopropyl alcohol is commonly found in rubbing alcohol. It is rapidly absorbed into body organs if ingested or through dermal exposure. It has roughly twice the toxicity of ethanol. Isopropyl alcohol is toxic even if small amounts of a solution with greater than 70% isopropyl alcohol is consumed (Viccellio, 1993).

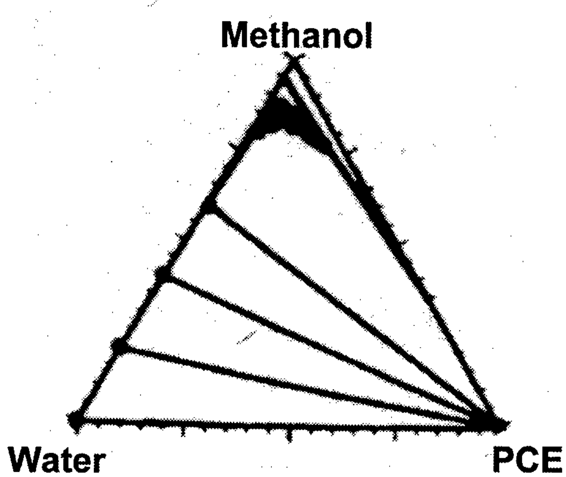
Tert-butyl alcohol (TBA) is also a clear, colorless fluid. It is commonly found as an additive to perfumes and fuels. It is a toxic substance if consumed in high concentrations. Breathing apparatus and protective clothing are recommended when handling the alcohol.

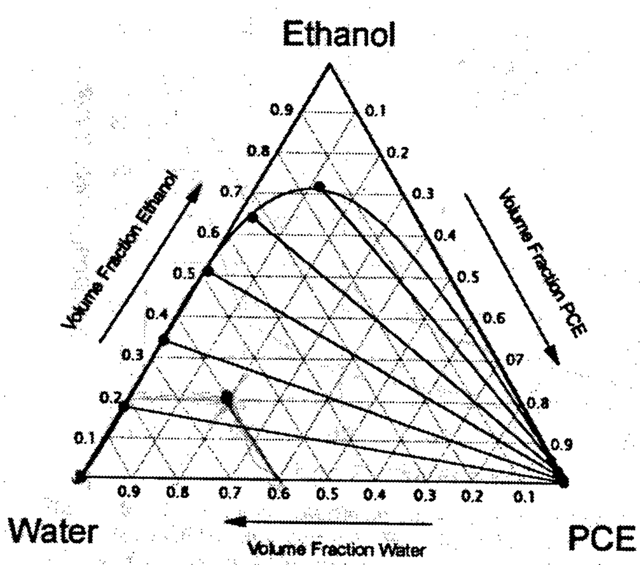
Alcohols at low concentration are thought to be highly biodegradable (Ward et. al., 1997). Significant losses due to biodegradation during cosolvent flooding are not expected, but low concentrations remaining after the flood are expected to degrade quickly over time. Alcohols at high concentrations are also flammable and explosive. This requires care to be taken during transport, handling, injection, and recycling of the alcohol. Table 1 lists critical properties of the cosolvents considered in this thesis.

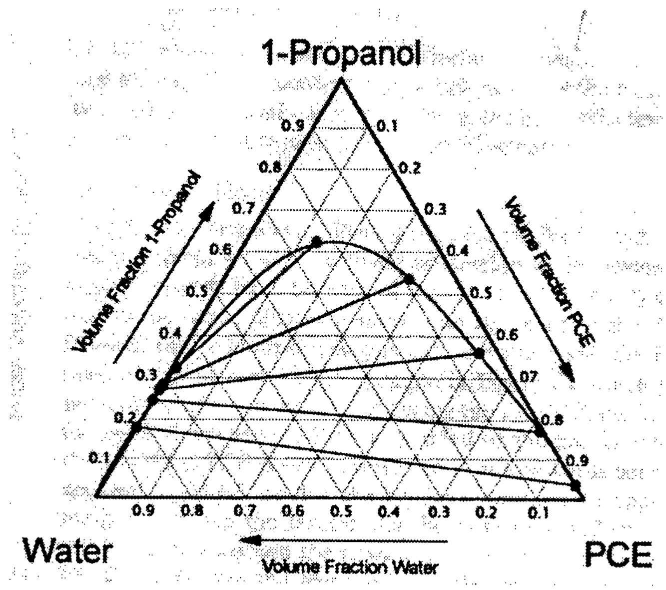
	Density	Cosolve Power Constant A*	Cosolve Power Constant B*	Molecular Weight	Interfacial Tension	Solubility
	(g/cm^3)	(unitless)	(unitless)	(g)	($10^3 Nm^{-1}$)	(mol/m^3)
Methanol	0.791	0.68	1.07	32.04	0.7	29.7
Ethanol	0.789	0.85	0.81	46.07	0.5	26.1
1-Isopropanol	0.804	0.89	0.63	60.08	---	24.9
2-Isopropanol	0.785	0.89	0.63	60.08	---	23.5
Tert Butyl Alcohol	0.823	1	0	74.12	---	23.1

Table 1. Critical cosolvent properties (Yalkowsky et.al., 1996, Lowe, 1996, Perry, 1979).
* Equation 3

Figure 8, shows the ternary diagram of each alcohol discussed in this thesis using PCE as the model DNAPL.


Methanol
Water
PCE


Ethanol
Volume Fraction Ethanol
Volume Fraction PCE
Water
Volume Fraction Water
PCE


1-Propanol
Volume Fraction 1-Propanol
Volume Fraction PCE
Volume Fraction Water
Water
PCE
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

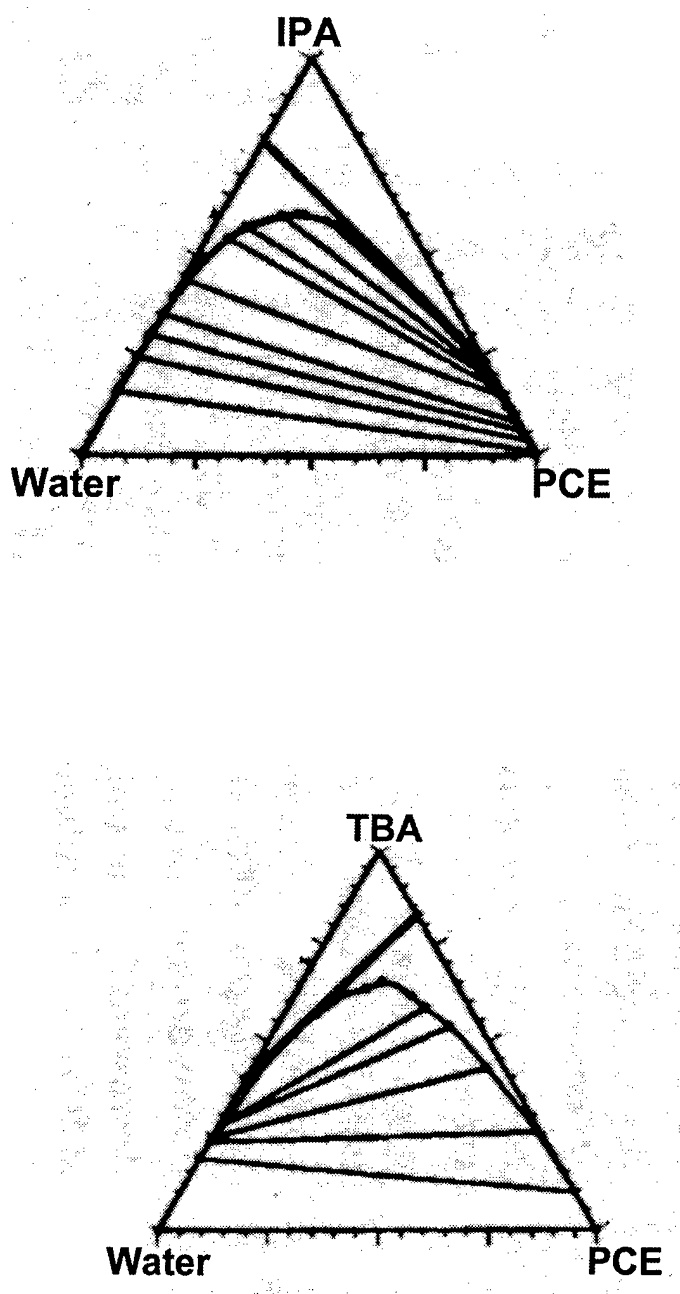


Figure 8. Ternary diagram of critical alcohols (Falta, 1998, Lunn and Kueper, 1997)

It is apparent that the five different alcohols behave differently in DNAPL-water-alcohol combination. Methanol, ethanol, and 2-isopropanol (IPA) exhibited type II(-) behavior. This behavior indicates that for this DNAPL-water-alcohol combination it is more suitable to solubilize the DNAPL than mobilize it. Mobilization could be accomplished using these alcohols, however it would require going outside the miscibility envelope, meaning that a large percentage of alcohol would be needed. 1-propanol and TBA exhibit Type II(+) behavior and therefore are more appropriate choices if mobilization of the DNAPL is desired.

2.3 Hill AFB Experiments

2.3.1 Hill AFB Background

In 1995, the first field experiment was performed using cosolvent flooding technology at Hill AFB. Hill AFB is located approximately 50 km north of Salt Lake City. The site selected was located within Operable Unit #1 and contained multiple contaminant sources that contributed to a large NAPL plume. Test cells were installed in the source area (Figure 9). The main source of the contamination was JP-4 jet fuel and degreasing solvents used during the 1940s and 1950s. 1,2-dichlorobenzene (DCB) and n-decane were the contaminants found in the highest concentrations, however, many other contaminants were detected (Enfield et. al., 1997). Table 2 lists the contaminants that were selected for monitoring during the field experiment.

The contamination rested in a shallow sand-gravel unconfined aquifer on top of a thick clay formation. The sand and gravel layer was approximately 6.1 meters thick, while the clay layer extended to depths of 90 meters or more (Enfield et al, 1997). The water table after installation of the test cells, was approximately 5.8 meters below the

ground surface. The highest concentration of DNAPL was located approximately 0.3 meters above the clay layer, which coincided with the regional water table position existing prior to the test cell installation. The DNAPL had penetrated less than 0.1 meter into the clay layer. The vertical distribution of the DNAPL was relatively constant between the 0.3 distance above the clay layer and 0.1 m below the clay layer.

A test cell was constructed to hydraulically isolate the area where cosolvent flooding was to be demonstrated. The cell used interlocking sheet piles driven approximately 3 meters into the clay unit (Figure 10). The joints of the sheet pile were sealed with a special grout to prevent leakage. The test cell had four injection wells, three extraction wells and 12 multilevel samplers. The layout and size of the test cell is shown in Figure 9.

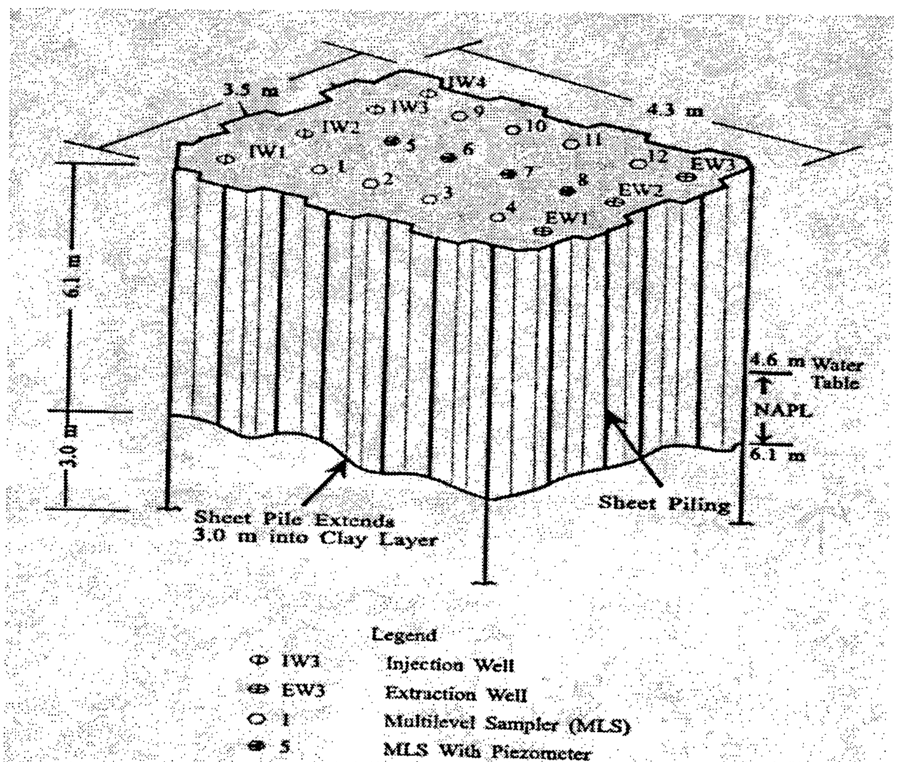


Figure 9. Layout of test cell used at Hill AFB (Enfield et. al., 1997)

The porosity of the aquifer in the cell was measured at 0.2, and the hydraulic conductivity was measured at 0.02 cm/sec. The addition of the hydraulic barriers allowed raising of the water table to 1m above the water table outside the test cell to permit passing the remedial fluid through the entire zone of contamination.

Before cosolvent flushing began, several tracer displacement experiments were conducted. Soil cores and groundwater samples were collected and analyzed to characterize the saturated zone of the aquifer. Next, a partitioning tracer was used to characterize the volume and distribution of the DNAPL. After this test, cosolvent flushing began. At the conclusion of the cosolvent flushing demonstration, another partitioning tracer was used to determine the performance of the cosolvent.

2.3.2 Field Experiment

Three different cosolvent mixtures were tested at Hill AFB. The first mixture contained a blend of 72% ethanol, and 28% water which was followed by a mixture containing 70%, ethanol, 12% n-pentanol, and 18% water. Ethanol was the primary flushing component, while n-pentanol was used to increase the solubility of the DNAPL. This flushing experiment was primarily used to mobilize the DNAPL, while a third mixture of TBA and water was also used to solubilize the DNAPL. Cosolvent flushing was conducted over a 10-day period followed by a 20-day period of flushing with water. A pumping rate of 3L/min was used, based on tracer testing which indicated this was equivalent to one pore volume per day. This rate was continued throughout the experiment except for two breaks. Cosolvent mixtures were distributed uniformly to the four injection wells using two pumps. The alcohol fraction in the injection fluid was

programmed to increase density overriding of the in situ water. One pump delivered the alcohol to the injection well, while the other delivered water.

In the three extraction wells, alcohol breakthrough occurred just prior to displacement of the NAPL. The initial sharp rise in alcohol concentration was followed by an extended period of tailing concentrations. Even after all water flushing was complete, a detectable level of alcohol still remained in the test cell. Some of the tailing could be due to alcohol being trapped in the capillary fringe of the aquifer. This occurs when denser water tends to go beneath the cosolvent mixture, which then becomes trapped in the capillary fringe. In the ethanol experiment, the partitioning tracer tests indicated over 97% of the NAPL was recovered. The TBA experiment displayed similarly promising results. Three weeks after the experiment, approximately less than 0.3% of the injected alcohol remained in the cell. At the end of the cosolvent flushing, the concentrations of the target contaminants in the extraction wells declined by at least 2 orders of magnitude. It is likely that continued flushing with a cosolvent mixture would have removed additional NAPL mass. Table 2 illustrates how much contaminant mass was actually extracted from the test cell.

Target Contaminant	Mass Extracted (kg)
1,1,1 Trichloroethane	0.0127
m,p xylene	0.203
1,2 Dichloroethane	1.326
1,3,5 Trimethylbenzene	0.385
n-Decane	1.863
n-Undecane	3.62

Table 2. Contaminant removed during Hill AFB demonstration of cosolvent flushing (Enfield et. al., 1997).

During the field experiments at Hill AFB, several test cells were setup similar to the one described above. This was done to test several different technologies side by side and compare their performance. It is apparent from figure 10, that both cosolvent mobilization and solubilization performed well compared to the other technologies.

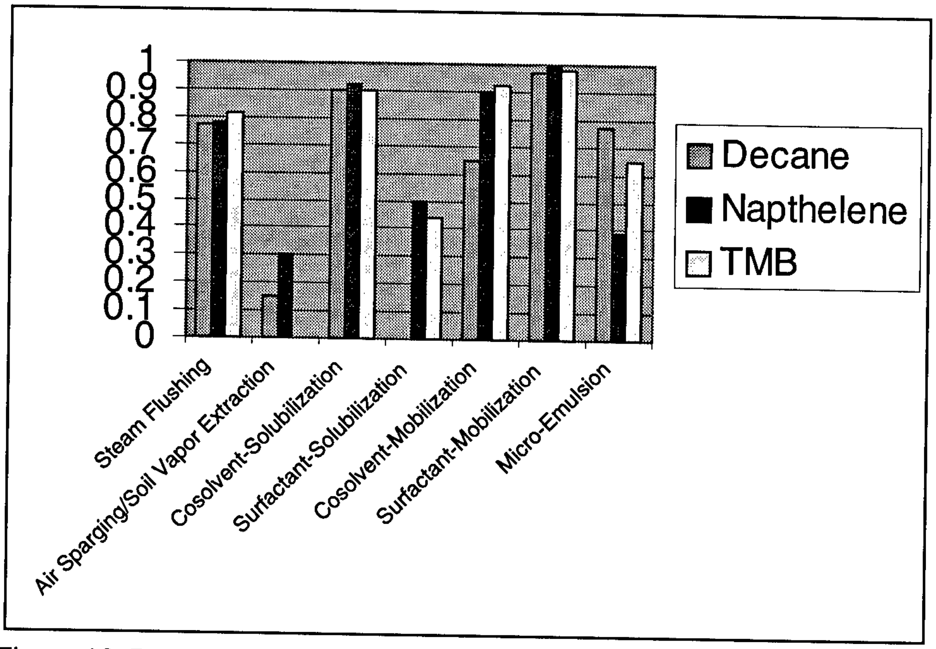


Figure 10. Data from Hill AFB experiments.

2.4 Cost of Cosolvent Remediation

The Hill AFB experiment demonstrated that cosolvents can be effective to remediate a DNAPL source area. The question remains, though, whether cosolvent flushing is a cost-effective alternative for DNAPL clean up?

A number of parameters must be determined in order to evaluate how much cosolvent flushing will cost. These parameters depend upon site characteristics and how the remediation is applied. Site characteristics include the depth and area of contamination, the type of contaminant present, the characteristics of the aquifer such as

hydraulic conductivity and porosity, and an estimate of the saturation of the contaminant in the soil. Operational parameters include the percentage of cosolvent added to the water, what type of cosolvent is used, the pumping rate of the cosolvent solution and whether or not the cosolvent can be recycled.

2.4.1 Site Characteristics

The first step to evaluating the cost of using cosolvents is to determine the volume of NAPL contamination present at the site in residual and pooled form. This can be extremely difficult because DNAPL typically migrates through tortuous pathways forming many small pools and zones of residuals. Typically a general region where the NAPL is believed to be may be identified (Cohen and Mercer, 1993). The DNAPL contamination volume is often influenced by several factors 1) the volume of DNAPL released, 2) area of infiltration, 3) time duration of release, 4) properties of the DNAPL, 5) properties of the soil, and 6) subsurface flow conditions.

Useful source of information for estimating the volume may come from interviews with present or former employees, records of chemical purchases, off-site water disposal, historical site engineering drawings, or archival aerial drawings (Cherry and Pankow, 1996). With this information, a rough estimate of the volume and area of contamination can be made. Information on the subsurface stratigraphy and DNAPL transport processes can help to refine the initial estimate.

The estimated volume of DNAPL and area of contamination can be further refined through invasive techniques such as drilling or through noninvasive techniques such as soil gas analysis. Drilling into the aquifer can provide evidence of the presence and distribution of the DNAPL. Abundant dark-colored DNAPL at high residual

saturation, or in layers and pools, is usually visible in soil cores. Ultraviolet florescence tests using methanol to prevent volatilization can be used to identify chlorinated solvents. Laser-induced fluorescence (LIF) is another in-situ method that can be combined with cone penetrometer testing (CPT) to produce continuous recordings of the stratigraphy which detects aromatic hydrocarbon contamination in the subsurface. LIF systems utilize a fiber optic laser assembly that emits a laser of a specific wavelength through a sapphire window in a CPT cone. When the laser encounters aromatic hydrocarbons, the contaminants fluoresce, which is measured by the sensors. Because LIF/CPT is quick, it may be possible to install a relatively large number of CPT holes to delineate the horizontal extent of the NAPL (Lowe, 1996).

Since drilling into the aquifer can lead to inadvertently mobilizing the DNAPL, other approaches may be used to characterize the contamination. These methods involve noninvasive techniques where measurements are made at or just below the ground surface using geophysical and soil gas surveying to characterize the area of contamination. This method is less costly, but provides less information about the contamination area. The ground penetrating radar test is based upon the fact that different subsurface materials have different dielectric properties. In the test, high-frequency electromagnetic waves are transmitted into the subsurface. Their reflection from interfaces between materials with different dielectric properties is monitored to evaluate the area of contamination. Another noninvasive technique involves electromagnetic conductivity. Electromagnetic conductivity methods measure the bulk electrical conductance of the subsurface by recording changes in the magnitude of electromagnetic currents that are induced in the

ground. These changes in currents reflect lateral soil variations, and the presence of conductive contaminants (Cohen and Mercer, 1993).

Partitioning tracers can also be used to locate and define the spatial extent of NAPL in the aquifer. In a partitioning test, two tracers are injected simultaneously into a suspected NAPL source area. One tracer partitions into the NAPL, while the second tracer does not interact with the NAPL. Injected tracers are then recovered from a nearby recovery well, and concentrations are measured as a function of time and flow rate. The tracer that partitions into the NAPL is transported more slowly through the test zone than the non-partitioning tracer. The extent of retardation of the partitioning tracer is an indirect measure of the average NAPL saturation, or volume, within the zone swept by the tracers (Sillan et.al., 1998).

Once the volume of DNAPL is estimated, the depth of contamination can also be predicted. If the volume released is small, the DNAPL may reside only in the vadose zone, since as the DNAPL sinks through the vadose zone a significant portion of the substance is trapped in the soil at residual saturation due to interfacial tension effects. Given only a small release, all the DNAPL may be trapped in the vadose zone and may never reach the water table.

If the volume released exceeds the capacity of the vadose zone the DNAPL will migrate through to the saturated zone. Once the DNAPL reaches the saturated zone it sinks beneath the water table until it reaches the confining layer of the aquifer and begin to spread out. A typical remediation site will have DNAPL saturation between 5 to 20%. If the saturation of DNAPL is greater than this, the DNAPL should be pumped out of the aquifer before a remediation technology is applied (Cohen and Mercer, 1993). Based on

the volume and area of contamination and the saturation percentage, the depth of DNAPL infiltration can be estimated. The smaller the contamination area the deeper the DNAPL will migrate into the subsurface. Also, the slower the contaminant is released the further the DNAPL migrates into the aquifer. If the DNAPL is spilt in large quantities quickly, ponding occurs. This creates tension forces within the DNAPL which allow it to remain on the surface longer (Cohen and Mercer, 1993) allowing the penetration depth of the DNAPL to be not as deep for the same time period as a smaller spill.

With the volume, area, and depth of contamination estimated soil cores can be taken. Soil cores provide information on the type of contaminants present and their concentration on a mass per mass basis, as well as providing information on soil characteristics such as grain size distribution, consistency and percent water saturation. Soil borings can also be used to get samples of NAPL for determination of NAPL density, interfacial tension and viscosity (Cohen and Mercer, 1993). Care must be taken when a boring or monitoring well installation intersects a DNAPL layer or pool because of the potential for further downward migration of the NAPL and expansion of the zone of contamination.

2.4.2 Operational Characteristics

Once site characteristics are identified, the user must select operational characteristics such as alcohol type and percentage. The model constructed for this thesis can then be used to calculate approximate flowrates and remediation costs.

To flush a DNAPL source area, a recharge/production well system as depicted in Figure 11 may be used. Note how streamlines from the recharge well flow through the zone of contamination and are recovered in the production well. The shape and width of

the capture zone are the results of the combined effects of draw down of the production well, mounding from the recharge well and the uniform regional flow. Let's assume the recharge and production wells are operated at the same flow rates. This flow rate is the most important engineered parameter for determining the width of the capture zone.

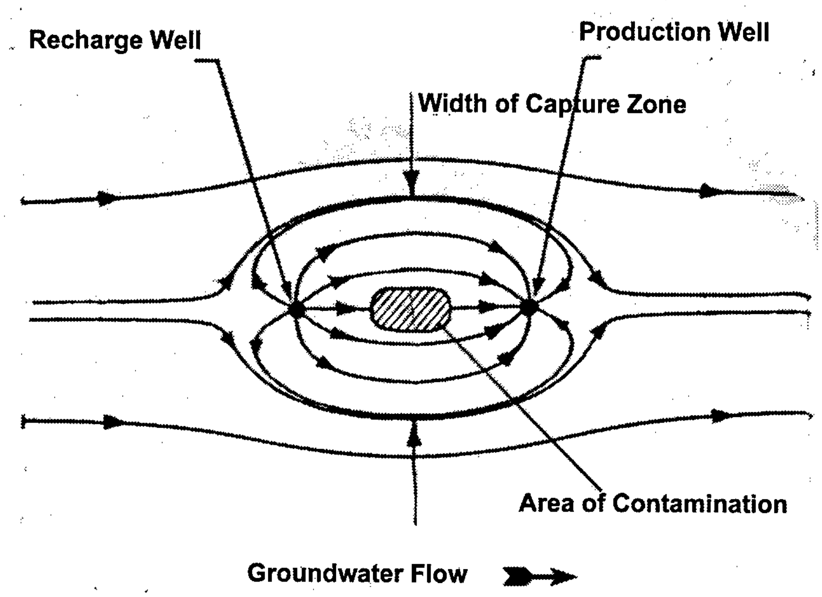


Figure 11. Plan view of capture zone model (Wilson, 1984).

If draw down is limited to 30% of the depth of the aquifer (b), the maximum pumping rate (Q_{max}) can be determined by the following equation (Bear, 1979),

$$Q_{max} = 2\pi * T * S / Ln(R/R_w) \tag{10}$$

$$R = 3000 * S * K^{1/2} \tag{11}$$

$$T = K * b \tag{12}$$

$$S = 0.3 * b \tag{13}$$

Where

T = Aquifer transmissivity (m^2/sec)

K = Aquifer hydraulic conductivity (m/sec)

b = Aquifer thickness (m)

S = Maximum drawdown (m)

R_w = Radius of well (m)

Once the maximum pumping rate is established the width of the capture zone (w) is calculated by solving the following equation (Wilson, 1984).

$$1 = T * J_o w/Q + (2/\pi) * \tan^{-1}(w/2a) \quad (14)$$

Where

a = Half the distance between wells [L]

Q = Pumping rate [L^3/Time]

T = Transmissivity [L^2/Time]

J_o = Regional hydraulic gradient [L/L]

After the maximum capture zone width is calculated, it is compared to the width of contamination. If the capture zone width exceeds twice the contamination width, the pumping rate is then incrementally decreased by 1% of the maximum pumping rate, until the calculated capture zone width is just under twice the width of the contamination. If the capture zone width is less than twice the area of contamination, another well pair is added, thus dividing the area of contamination treated by the well pair in half. This model assumes the maximum area of contaminates to be treated by a single well pair is 50 by 100 meters as recommended by the EPA (Enfield, 1998). If the contamination area is larger than this, the model divides the contamination area into subsections smaller than 50 by 100 meters. The model also assumes that only a single well pair will be operated at

a time. This eliminates the additive draw down effects due to multiple wells operating simultaneously.

2.4.3 Well Operation Costs

As seen in figure 11, a production (extraction) and recharge (injection) well pair will be used in each area. This model assumes that the cost of installing each well is $10,000. Monitoring well costs are not included in the model, since monitoring of the site is necessary no matter which remediation technology is chosen. However, well materials only account for a fraction of the costs. Operating the well must also be accounted for. The following equation is used to calculate total annual pumping cost (TPC) to operate the wells (Christ, 1998).

$$TPC = P*N*Cost_p/\eta \tag{15}$$

$$P = \gamma*H*Q \tag{16}$$

Where

TPC = Total annual pumping costs [$/yr]

P = Power used to lift water [$M\text{-}L^2/T^3$]

Q = Annual flow rate in each well [L^3/yr]

γ = Specific weight of water [$M/L^2\text{-}T^2$]

H = Distance to water table [L]

N = Number of wells

$Cost_p$ = Cost of electricity [$\$M^{-1}L^{-2}T^2$]

η = Pump efficiency

The model assumes the cost of electricity is $.045/kwh, since this is what a large government user, such as an Air Force Base is currently charged.

2.4.4 Alcohol Costs

Once the well costs and pumping rates are determined, the cost of alcohol needed to remediate the area of contamination by cosolvent flushing is calculated. Alcohol costs vary depending on the alcohol chosen. Table 3 lists the cost per gallon for the five alcohols considered in this thesis.

Methanol	0.45
Ethanol	1.75
1-Isopropanol	2.502
2-Isopropanol	1.975
Tert Butyl Alcohol	3.08

Table 3. Cost of alcohol ($/gal) (Cost quotes obtained from Union Carbide and Ashland Chemical Company, 1999).

Obviously, the higher the percentage of alcohol chosen, the more alcohol will be required. The alcohol costs for flushing one pore volume through a capture zone volume (IPA) may be calculated as follows:

$$IPA = Cost_a * \theta * ACZ * b * N/2 * (Percent_a/100) \quad (17)$$

Where

IPA = Alcohol costs for flushing a single pore volume ($)

$Cost_a$ = Cost of the Alcohol ($\$/L^3$)

θ = Aquifer porosity

ACZ = Area of capture zone based on calculated capture zone width and distance between the well pairs (L^2)

b = Aquifer thickness (L)

N = Number of Wells

$Percent_a$ = Percentage of alcohol being used in cosolvent mixture

Unfortunately flushing a single pore volume is inadequate for total remediation of a contaminated zone. If new alcohol must be introduced in to the aquifer to satisfy flushing requirements for multiple pore volumes, it is likely the technology will not be cost effective (Lowe, 1996). Therefore, the ability to recycle the cosolvent and re-inject it back into the aquifer is critical.

2.4.5 Cosolvent Recycling

There are several suggested ways to recycle cosolvents including pervaporation, evaporation, solvent extraction, distillation, or air stripping.

Pervaporation is a selective membrane separation technique. Pervaporation systems concentrate the mixture as it separates the different components. It is used successfully to separate alcohol and contaminant in commercial industries worldwide (Dutta et. al, 1997). In a pervaporation process, the component to be separated preferentially absorbs on one side of a dense polymeric membrane. The liquid, such as an alcohol, diffuses through the membrane. As the liquid moves through the membrane it vaporizes and must be condensed again for recycling. The major advantages of pervaporation are that it is energy efficient because only the fraction of the feed that diffuses through the membrane is vaporized. However, a lot of energy is required to move the liquid through the membrane. The remainder of the solution does not undergo any phase change. Unlike distillation, pervaporation does not require recycling the entire mixture back into the process in order to achieve better separation. The equipment

required for the process is compact and easy to maintain and operate. Lastly, pervaporation equipment can be used on any size remediation project whether large or small (Dutta et. al, 1997).

Pervaporation however is a slow, time consuming process. It may be difficult to obtain a large membrane of the right type that can handle the type of fluids and flow rates required by cosolvent flushing remediation. Large size membranes are extremely expensive and rare. They are also easy to flood rendering the membranes useless. Membranes are the most critical items in a pervaporation system design (Dutta et. al, 1997). Although most membranes have the ability to effectively remove alcohol from another substance such as water, this separation is limited to systems where there is only 10% alcohol or less, or to purify an alcohol system when the alcohol is greater than 90% (Geankoplis, 1993). Alcohol solutions between 10-90% causes swelling of the membrane, rendering it ineffective. Since cosolvent technology typically requires alcohol percentages above 10%, pervaporation will not be considered as an option. Pervaporation also has high capital costs, operational costs, labor-intensive assembly, and leakage problems due to the large number of gaskets in the system (Dutta et. al, 1997). These problems make pervaporation not as cost effective as other separation alternatives.

Another way of recycling a cosolvent involves evaporation. Evaporation concentrates nonvolatile solutes and solids by evaporating water and volatile compounds. During evaporation the mixture is heated to the alcohol's boiling point. The alcohol vapors released by the evaporator need to be condensed, so the alcohol can be recycled and reused. The concentrated liquid remaining after evaporation will typically be drummed and sent off site for disposal. The process is usually done at very small sites

where only a few thousand gallons of fluids per day are handled. This is because at larger sites the time required to evaporate the compounds greatly increases, as does the cost of the required evaporation equipment (Lowe, 1996). The evaporation process is essentially the same process used in batch system distillation only in lower amounts. Therefore, the costs of evaporation will be examined under the distillation section.

Solvent Extraction involves mixing an additional solvent into the mixture to be separated. The solvent mixes with the organic compounds in the mixture allowing the alcohol to be removed from the mixture. The solvent creates greater separation between the alcohol-water-NAPL mixture by affecting the vapor-liquid relationship between water and alcohol. The solvent usually has a high boiling point and can raise the boiling point of water creating a greater separation between the water and alcohol during distillation. Since distillation is still required to separate the alcohol from the mixture, this method is not more cost effective than distillation alone since it also requires an additional solvent to work.

The main method of recycling cosolvents is through distillation. Distillation is currently used more than 80% of the time in industry to separate alcohol from other liquids (Tham, 1997). A distillation system separates the DNAPL from the alcohol based upon differences in vapor pressures between the components that make up the mixture. At a given, fixed temperature, one component in a mixture has a higher vapor pressure than the other and therefore is more volatile. This is usually the alcohol in an alcohol, water, and DNAPL system. However depending on the alcohol and DNAPL being separated this is not always the case. Table 4 lists the boiling points of the DNAPLs and alcohols considered in this thesis. As can be seen, carbon tetrachloride

boils at 76.7 degrees C, while 1-isopropanol boils at 97.8 (Chilton and Perry, 1979). Since carbon tetrachloride boils at a lower temperature than the alcohol, using a distillation system would only separate the carbon tetrachloride. If this situation occurs, recycling of the alcohol is not possible. Distillation also would not be the most cost efficient way to remove carbon tetrachloride from the solution. In these circumstances air stripping is more cost effective than distillation. The greater the difference in boiling points and therefore vapor pressures between each of the compounds, the easier the separation is for the distillation column.

Alcohol	Boiling Pt (C)	DNAPL	Boiling Pt (C)
Methanol	64.7	Chloroform	62
Ethanol	78.4	Trichlorofluoromethane	290
1-Isopropanol	97.8	Carbon Tetrachloride	76.7
2-Isopropanol	82.5	1,2 Dichloroethane (DCA)	83.5
Tert Butyl Alcohol	82.9	1,1,1 Trichloroethane	113.7
		Trichloroethylene (TCE)	87.2
		Tetrachloroethylene (PCE)	121.4
		Chlorobenzene	132
		Dicholorbenzene	172
		1,1,2,2 Tetrachloroethane	146.4

Table 4. Table of boiling points (Chilton and Perry, 1979).

During distillation, the mixture to be separated enters a distillation column. This mixture is then heated. As distillation of the alcohol occurs, the alcohol vapor will have a greater concentration of alcohol than the original mixture entering the distillation column. As the vapors move up the distillation column, the vapor contains a greater portion of alcohol. This vapor is then condensed, and the alcohol can be reused. The high boiling

components such as water and DNAPL are disposed of through a bottom feed. As the vapor becomes richer in volatile components, the liquid becomes richer in the less volatile components. An illustration of a typical distillation column is seen in figure 12.

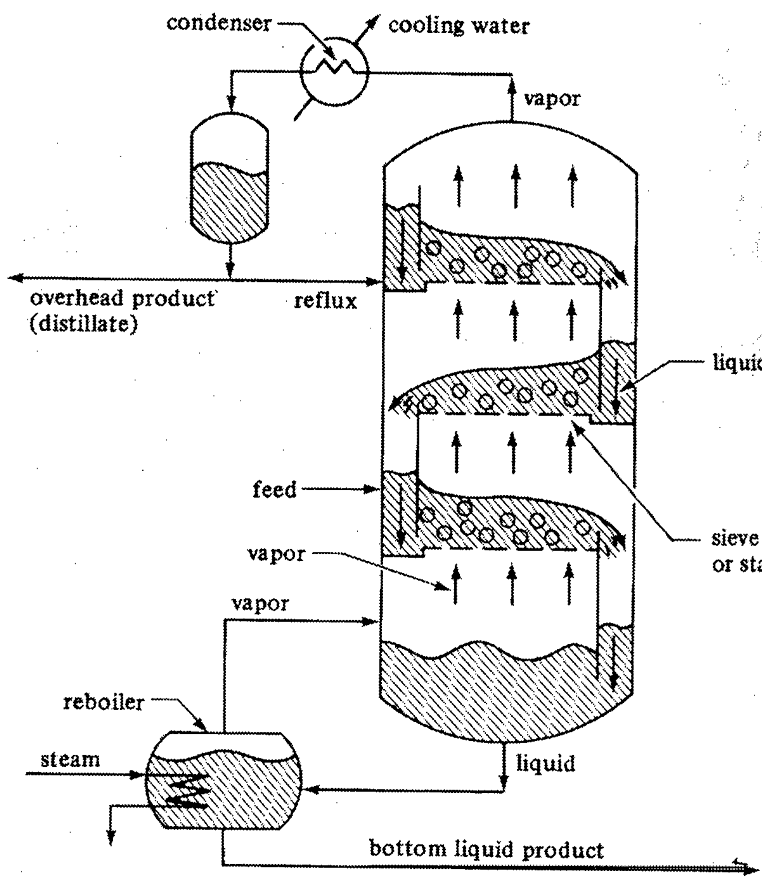


Figure 12. Typical distillation system (Geankoplis, 1993).

A distillation column system can be either extractive, which requires adding a solvent, or be a two-product distillation system. Extractive distillation has less equipment requiring fewer stages to remove the alcohol from the system, but the equipment is more complex and costly. Extractive distillation requires a distillation column, an evaporator, heat pump, solvent and a spray drier to operate (Rouseeau, 1987). Two-product

distillation columns simply require a column, reboiler, condenser, and several pumps (Rousseau, 1987).

The separation of alcohol from water in a distillation system poses an additional problem since an azeotropic mixture may be created. An azeotropic mixture is a mixture of two or more volatile components that have identical compositions in the vapor and liquid phases at a minimum boiling point. In an azeotropic mixture, the minimum boiling point for the mixture of the two components is below the boiling point for either pure compound. Such a system if not properly handled could boil away the entire liquid at a constant pressure without separating the two compounds. These special systems must be handled one of three ways. They can be distilled at a pressure that eliminates the azeotrope, distilled using two columns at different pressures, or distilled by adding other compounds such as solvent that alter the relative volatility of the original components (Nisenfeld and Seeman, 1981). When a solvent is added to the mixture to be separated, the solvent forms an azeotrope with one of the original components. The boiling point of this azeotrope must be different enough from the remaining components to make distillation possible. Azeotropes need to be avoided since they greatly increase the cost to separate the liquids (Saliba, 1998). This means that the purity of the recycled alcohol is limited by the mole fraction at which an azeotrope forms. Methanol forms an azeotrope with water at 99%. Therefore, methanol can be distilled to almost 99% purity. Ethanol forms an azeotrope with water at 95%. This means that 5% of the mole fraction of the alcohol being recycled from the distillation column will contain water-NAPL mixture. 1-Isopropanol and 2-isopropanol form azeotropes at 87%, while TBA forms an azeotrope at 88% (Hala et. al., 1968). This means that the solution recovered from distillation of

TBA, 1-isopropanol, and 2-isopropanol will not be as pure as that recovered from ethanol and methanol.

Distillation of alcohol can be accomplished through a batch system or continuous column system. Batch distillation systems are ideal for smaller jobs since they require more time to remove alcohol as the flow of feed increases (Robinson, 1950). Both distillation processes require large amounts of energy and therefore have high operating expenses associated with them (Nisenfeld and Seeman, 1981). They are however becoming more energy efficient as equipment improves. Continuous column systems are capable of removing alcohol with great efficiency. They are also capable of handling large flows and mixtures with a high percentage of alcohol (Niesenfeld and Seeman, 1981). Continuous distillation requires a constant source of both heating and cooling which drives up the cost. However, money is saved in the overall operating costs since the system only has to be completely heated at the beginning of the operation. After start up, only intermittent heat is required to keep the compound at a specific boiling temperature. Continuous distillation systems also offer uniform quality output since the system remains at constant load, temperature and pressure while in operation. The selection of distillation system (batch or column) should be made based upon the operation being performed (Saliba, 1998). For cosolvent remediation, continuous columns are most appropriate due to the steady flow of alcohol-water-NAPL mixture extracted from wells. A constant pumping rate of fluid can be immediately distilled in a distillation column, thereby allowing the recycled alcohol to be reinjected back into the aquifer.

Air stripping is another suggested method for recycling alcohol. Air stripping is a mass transfer process that also relies on the transfer of compounds from the water phase to the gas phase. Air stripping is one of the most commonly used processes for remediation of extracted groundwater contaminated with volatile organic compounds. Air stripping is used successfully to remove volatile contaminants from water with 99% efficiency (Vogel and Lundquist, 1994). If removal efficiencies higher than 99% are desired, air stripping towers can be operated in series by recirculating the water from the first tower to the feed inlet of the second tower. An air stripper is designed to strip chemicals with the highest Henry's Law Constant first at a specific temperature. Air stripping however is complicated by the presence of cosolvents. Since most alcohols are extremely volatile substances, it is difficult to use an air stripper to recycle the alcohol. This is because the affinity between the alcohol and water cause the Henry's constant of the alcohol to be low. This method is not used to separate alcohol from water, and therefore no studies have been conducted looking at this as a possible separation technology. Air stripping however can be used to separate dissolved DNAPL from water coming off the bottom feed of the distillation column. This is an effective way to minimize disposal costs.

2.4.6 Distillation Column Design

From the previous section, we've found that distillation appears to be the most practical method of recycling alcohol. Distillation columns are designed using vapor-liquid equilibrium (VLE) data from laboratory studies. The VLE characteristics of the

mixture will determine the number of stages or trays required to separate the alcohol in a column. Figure 14 illustrates a generic liquid-vapor equilibrium curve. The model developed in this thesis calculates a VLE based on laboratory information from Hala et. al., in 1968.

The most common method to design distillation columns is the McCabe-Thiele design method (Tham, 1998). The McCabe-Thiele approach is a graphical one, and uses the VLE diagram to determine the theoretical number of plates required to separate a binary mixture. Since most alcohol-water-DNAPL mixtures extracted from the wells contain less than 1% DNAPL, this thesis assumes the main separation will occur between the alcohol and the water. For this reason, it is assumed that we are dealing with a binary mixture composed of alcohol and water. The McCabe-Thiele method assumes constant molar overflow. This means that the molal heats of vaporization of the components (water and alcohol) are roughly the same. Other assumptions are that the heat effects from heats of solution, and heat losses to and from the column are negligible, and for every mole of vapor condensed, 1 mole of liquid is vaporized.

The first stage in using the McCabe-Thiele method is to convert the flow of the mixture to be separated, also known as the feed, into mole fractions. This is done using the following equations:

$$X_f = (Alcohol_f)/(Total_f) \tag{18}$$

$$Alcohol_f = (Fraction_a * Q_d)/(Molecular_a) \tag{19}$$

$$Water_f = (1\text{-}Fraction_a * Q_d)/(Molecular_w) \tag{20}$$

$$Total_f = Alcohol_f + Water_f \tag{21}$$

Where

X_f = Mole fraction of alcohol in feed

$Alcohol_f$ = Alcohol feed rate (lb moles/time)

$Water_f$ = Water feed rate (lb moles/time)

$Fraction_a$ = Fraction of alcohol in solution

$Molecular_a$ = Molecular weight of alcohol (lb/mol)

$Molecular_w$ = Molecular weight of water (lb/mol)

Q_d = Pumping rate of well (lbs/time)

Once the feed composition is determined, the molar fraction of alcohol in the distillate (x_d) and the bottom of the column (x_b) may be calculated.

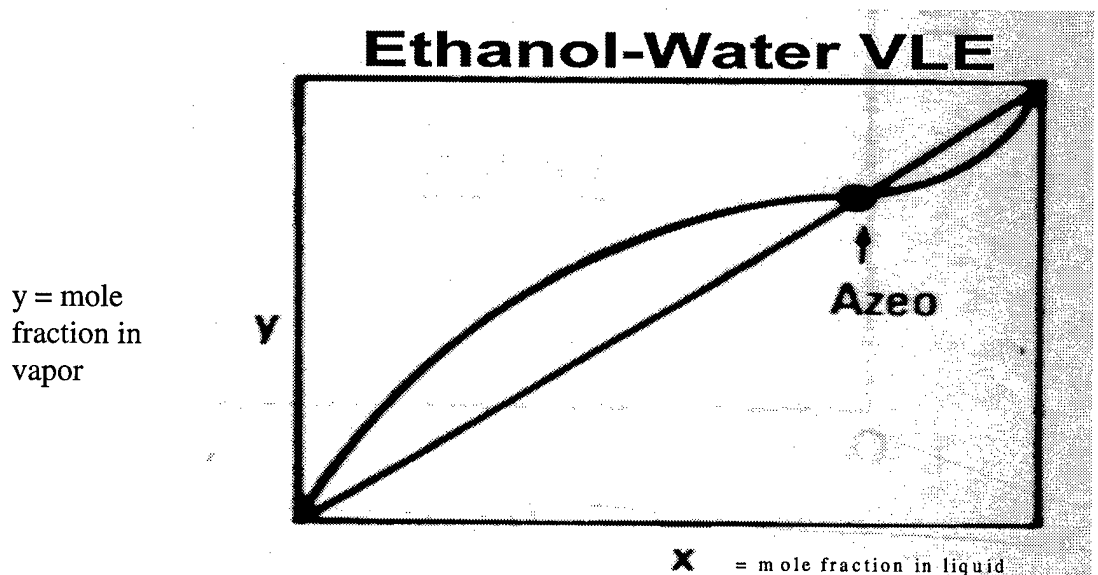


Figure 13. Ethanol-water vapor-liquid equilibrium diagram (Rousseau, 1987).

These fractions are dictated by the mole fraction at which azeotropes formed (figure 13).

As can be seen in figure 13, it is difficult to separate this water-ethanol for a mole fractions of ethanol greater than Azeo. This is because at mole fractions greater than

Azeo, the alcohol-water mixture crosses the equilibrium line. This means that under these conditions the boiling point of the water and alcohol mixture becomes lower than alcohol alone, and therefore the alcohol cannot be separated. Table 5 lists the distillate and bottom mole fractions of the alcohols considered in this thesis.

Based on the azeotropes and laboratory results from Hala et. al., (1968), the model calculates a VLE relationship for the given binary mixture of alcohol and water. This VLE relationship allows the computer to compute the graphical representation of the VLE curve such as in figure 14.

$$y = (\alpha * x)/(1+(\alpha-1)*x) \qquad (22)$$

Where

α = Equilibrium constant

x = fraction in liquid phase varying from 0 to 1

y = fraction in vapor phase varying from 0 to 1

Table 5 lists the equilibrium constants (α) for the alcohol-water mixtures considered in this thesis.

	Xd	Xb	α
Methanol	0.99	0.01	0.5051
Ethanol	0.95	0.05	1.8241
1-Isopropanol	0.87	0.13	0.9755
2-Isopropanol	0.87	0.13	1.0117
Tert Butyl Alcohol	0.88	0.12	1.1204

Table 5. Alcohol properties for distillation (Hala et. al., 1968 and Chilton and Perry, 1979)

Given the VLE relationship in Table 5, the model goes through the following calculations to determine the number of plates required in a distillation column for mixture separation. Although this is a graphical method, the model uses equations to generate all of the necessary information to determine the cost of a distillation column.

First the operating lines of the distillation column must be determined. The operating lines define the mass balance relationships between the liquid (x) and vapor (y) phases in the column. There is one operating line for the bottom or stripping section, and one for the top (rectification or enriching) section of the distillation column. The operating line for the rectification section is constructed as follows. First, the desired top product purity (X_d) is located on the 45-degree line. This is point A in figure 14. A line with a minimum reflux ratio slope is then drawn from point A until it intersects the q line. This is point B. The minimum reflux slope is determined by taking the change in the vapor over the change in liquid between the composition the material is distillated at and the composition it is being fed into the column at. At point A, $X_d = Y_d$, therefore the change in vapor composition is equal to the difference between vapor being distilled and the vapor brought into the feed. The change in liquid composition is determined by the difference between the feed at equilibrium and the feed on the VLE diagram. The minimum reflux ratio determines the minimum ratio of flow that is recycled back through the column to flow being distilled. It is calculated using the following equation from Rousseau (1987).

$$R_{min} = (X_d - Y_f)/(Y_f - X_f) \tag{22}$$

Where

R_{min} = minimum reflux ratio

X_d = Mole fraction of alcohol in the distillate

$*Y_f$ = Mole fraction of alcohol in the form of vapor in the feed

X_f = Mole fraction of alcohol in the form of liquid in the feed

$*Y_f$ is obtained by substituting X_f calculated in equation 17 into equation 21.

The q line ensures that the McCabe-Thiele method will not require an infinite number of steps to perform the required mixture separation. The q line also determines where the feed should flow into the distillation column since it coincides with the intersection of the operating and enriching lines as seen at point C on figure 14. Using figure 14, as an example the flow would be introduced in the fifth plate, since there are five horizontal lines between points A and B. The condition of the feed is also determined by q. If q is between 0 and 1 the feed is a mixture of liquid and vapor. If q is greater than 1 the feed is a subcooled liquid, and if q is less than 0 the feed is a superheated vapor.

The following equation calculates q to determine the condition of the flow entering the distillation column. This calculation is necessary to determine where the q line will cross the VLE curve (point C).

$$q = ((H_v - H_l) + c_{pl}*(T_b-T_f))/(H_v-H_l) \quad (23)$$

Where

$H_v - H_l$ = Latent heat of the mixture (BTU/lb-mol)

c_{pl} = Heat capacity of the mixture (BTU/lb-mol-F)

T_b = Boiling point of the alcohol (F)

T_f = Inlet feed temperature (F)

After the rectifying line is calculated, the stripping line is then drawn. The stripping line connects X_b located on the 45-degree line (point D, figure 14) to the intersection of the q-line and the rectification line (point B, figure 14).

Finally the number of plates required for the separation can be determined. The number of plates is calculated by counting the number of horizontal lines drawn between the VLE curve and the two operating lines (figure 14). The theoretically required number of plates is one less than the number of horizontal lines shown since the McCabe-Thiele method includes contribution of the reboiler in carrying out the separation. In figure 14, the required number of plates to perform the separation is 8.

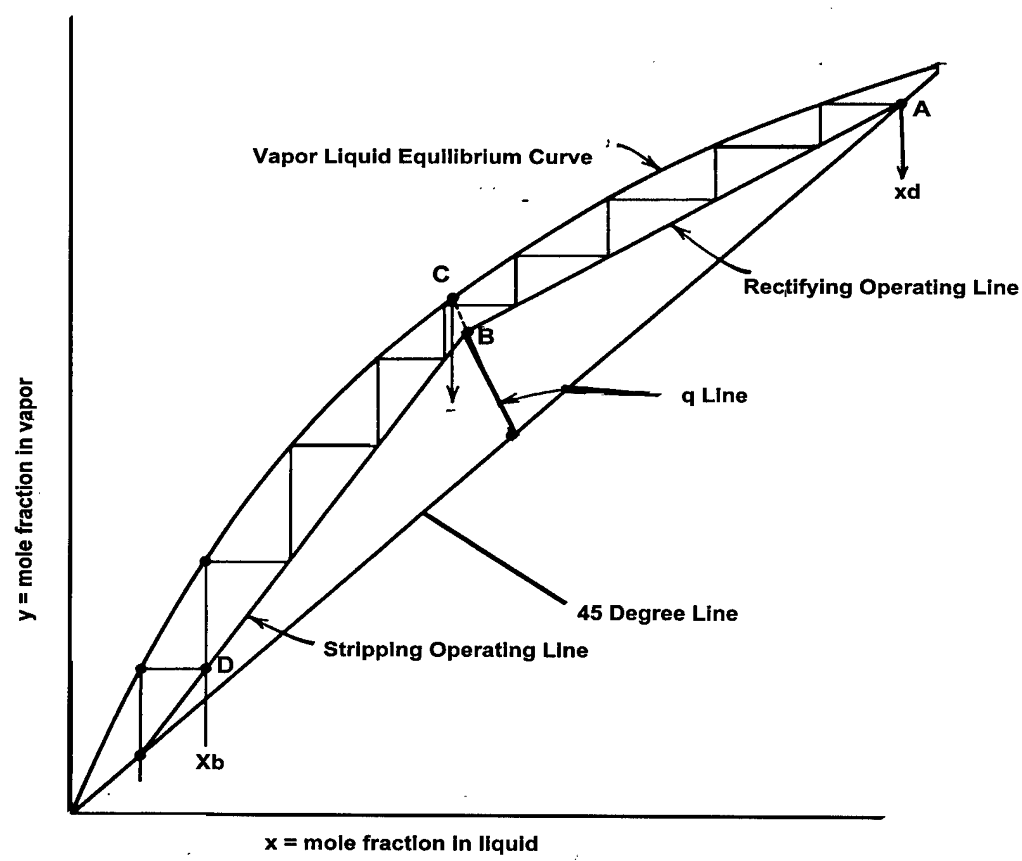


Figure 14. Generic vapor-liquid equilibrium curve (Rousseau, 1987).

The actual number of plates is determined by dividing the theoretical number of plates by an efficiency factor. The efficiency factor ranges from .5 to .85 depending on the type of plate used. This model assumes that bubble cap plates will be used since they are the most common and easiest to acquire. A midrange efficiency of .7 was assumed. Once the number of plates are determined the costs associated with building a distillation column can be calculated. The method used by the thesis model to determine the cost of distillation is included in the Appendix.

2.5 Comparison of Cosolvent and Surfactant Flushing Costs

Once a cost estimate for cosolvent flushing is complete, it shall be evaluated against other technologies. This will help determine if cosolvent remediation is a cost-effective option. Let us look at some of the costs calculated for surfactant flushing, perhaps the primary competitor to cosolvent flushing, for remediating DNAPL source areas (Harwell et. al., 1995).

In his economic analysis of surfactant enhanced pump and treat remediation, Harwell found that large quantities of surfactant-water mixture can be used to cost-effectively remediate a DNAPL source area using surfactant flushing. Using a source area ranging from 10 acres to ¼ acre, Harwell calculated cost and time needed to remediate the source area, as seen in table 6. In his cost estimate, Harwell assumed the porosity of the soil to be 30%, and the saturation of the DNAPL to be 13%. He also assumed the source of contamination contained 198,000 lbs TCE, 220,000 lbs PCE, and 171,000 lbs DCA. He also assumed the contamination had reached a depth of 20 feet.

Harwell estimated that 68 wells were necessary for the remediation. Table 6 displays the results of his study.

	Years to Remediate	Cost in $1000's
No Surfactant	25	$1,700
Surfactant to 10 Acres	2	$8,700
Surfactant to 1 Acre	2	$1,900
Surfactant to 1/2 Acre	2	$1,500
Surfactant to 1/4 Acre	4	$1,400

Table 6. Time and cost of surfactant remediation (Harwell et. al,, 1995).

Next, a cost estimate of both surfactant and cosolvent remediation will be reviewed. Unlike Harwell, Lowe (1996) used Remedial Action Cost Engineering and Requirements (RACER) software to evaluate his costs. RACER is an environmental cost estimating system produced by the Air Force for evaluating environmental projects.

Lowe estimated the cost of remediating a small site that originally contained 1,000 55-gal drums that spilled in the 1960's. These drums held 80% TCE, 5% PCE, and 15% waste oil and grease. The release covered a DNAPL area of 1 acre, and reached a depth of 6 m in the aquifer. The aquifer was assumed to have a porosity of 30%. Lowe estimated remediation of this site using both surfactants and cosolvents and compared the price difference. Using surfactants, he estimated that he would need to flush with 4 pore volumes of 4% surfactant plus 4% isopropyl alcohol and sodium chloride. He assumed the surfactant would be recycled but the alcohol would not be. The isopropyl alcohol was used to ensure the DNAPL did not mobilize downward. Using cosolvents, Lowe assumed he would flush with a 90% ethanol-water solution. Surfactant and cosolvent systems both used 25 chemical injection wells, 40 recovery wells, and 4 gradient control

wells. Both sites were flushed with water, followed by either surfactant or cosolvent flushing. For the surfactant flood, the 4 pore volumes were flushed over 1 year period while the cosolvent flood required 1 pore volume of alcohol flooding over 39 days. The alcohol solution was added at a rate of 34.6 m^3/d, while the surfactant solution was added at a rate of 170 m^3/d. Water flooding after the flushing was included in both estimates. It was assumed that there was no method of recycling the alcohol. Therefore all the waste generated in the cosolvent flood would have to be disposed of. This made the disposal costs for alcohol flooding the most significant cost, causing alcohol flooding to be less cost effective than surfactant flooding. Table 7 shows the costs of surfactant and alcohol flooding.

	Case Description	Capital	O&M	Total Project Cost
Surfactant	1 Acre Base Case	3,990,000	3,170,000	6,940,000
	1 Acre Min Cost[1]	1,330,000	770,000	2,030,000
Cosolvent	1 Acre Base Case	3,100,000	4,530,000	7,410,000
	1 Acre Min Cost[1]	1,100,000	1,710,000	2,730,000

Table 7. Cost of cosolvent remediation (Lowe, 1996)
[1]Same as base case but a more efficient system is used that allows a lower cost treatment system, labor, utilities, analytical and incineration costs.

As a result of his study, Lowe concluded that alcohol flooding is not as cost effective as surfactant flooding. He felt the only way to make cosolvents cost effective is to recycle the alcohol. Lowe's estimate for surfactant costs were very close to the costs reported by Harwell (compare Table 6 with the 1-acre min cost for surfactant in Table 7).

2.6 Legal Aspects of Remediation

This thesis will look at the cost-effectiveness of cosolvent remediation. However, in order to be implemented the technology must comply with federal, state, and local laws and regulations that govern environmental remediation. The primary federal law used to regulate the process is the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

CERCLA is the basis for a national program for responding to releases of hazardous substances to the environment. CERCLA establishes the procedure for identifying and cleaning up contaminated sites may present an imminent and substantial danger to public health and welfare.

Under CERCLA, the EPA has developed a systematic set of performance evaluation criteria for use by site managers for selecting a remediation technology. The criteria are derived from requirements found in the National Contingency Plan (40 CFR 300) and CERCLA sections 121 (b) and 121 (c). The criteria are designed to provide structure to the technology selection process and to capture the full range of performance issues associated with an environmental site remediation project (Skumanich, 1994). During a site remediation project, the EPA uses the six-step remedial process shown below.

CERCLA National Cost Planning Process (NCP)

1. Site Discovery
2. NPL Ranking and Listing
3. Remedial Investigation/Feasibility Study
4. Record of Decision
5. Remedial Design
6. Remedial Action

During the remedial investigation/feasibility study step of the NCP process, information needed to evaluate the usefulness and effectiveness of different environmental remediation technologies is gathered. Then, by applying the CERCLA performance criteria, an assessment is made as to how well each potential technology will perform at the particular site under investigation. The selection of a technology is recorded in the Record of Decision (ROD) along with a detailed explanation of why the selection was made (Skumanich, 1994). The nine performance criteria identified by the EPA used to select an environmental remediation technology are listed below.

<u>CERCLA Technology Performance Criteria</u>

1. Overall protection of human health and the environment
2. Compliance with all other applicable or relevant and appropriate requirements (ARARs)
3. Long-term effectiveness and permanence
4. Reduction of toxicity, mobility, or volume through treatment
5. Short-term effectiveness
6. Implementability
7. Cost
8. State acceptance
9. Community acceptance

The first two criteria are threshold criteria. Any technology selected for use at a particular site must fully satisfy these criteria to be acceptable. The overall protection of human health and the environment is important in determining whether the technology will function in a safe manner that will provide adequate protection to human health and the environment. It therefore is closely related to other criteria, especially long-term effectiveness and permanence, short-term effectiveness, and compliance with ARARs. Because of this relationship, a technology that is assessed to perform well relative to the

other criteria should be able to satisfy this encompassing criterion of overall protection of human health and the environment.

The second threshold criterion is compliance with ARARs. This criterion is used to determine how well a proposed environmental remediation technology complies with federal, state and local environmental laws. This criterion has the objective of ensuring that no other environmental requirements are violated during a remediation project. The use of cosolvents has not yet as of 1999, been proposed to any state as a remedy. One state, Idaho, has approved a demonstration in a controlled cell, as of 1996. Cosolvents have since been used in similar demonstrations at Hill AFB, in Utah (Enfield et. al., 1997), and are being proposed for use at Dover AFB, in Delaware. Surfactant injection has been approved in eleven states as of 1996 (United States Environmental Protection Agency, 1996). No state has unequivocally banned injection technologies for treating subsurface contamination though most states prohibit injecting substances that will cause an aquifer to violate ground water quality criteria. Currently, however there are no identified maximum contaminant levels for alcohol in groundwater. It is therefore left up to each state to determine whether to permit cosolvent flushing on a case by case basis (United States Environmental Protection Agency Hotline, 1998). Other reasons for states rejecting the use of injections are: (1) the technology as presented to the state fails to adequately demonstrate a monitoring and recovery plan, (2) the plan lacks a clearly defined remediation procedure, or (3) the state lacks experience with injection projects. Almost all states rely on the project work plan to decide whether to approve a remediation technology requiring injections. Several states require a closed system or some evidence

that all injection will be captured and removed (United States Environmental Protection Agency, 1996).

Summary of State Policy and Experience with *In Situ* Ground Water Remediation

State	Regulatory Prohibition (Yes/No):	Policy Prohibition (Yes/No):	Proposal Reviewed (Yes/No):	Injection Allowed (Yes/No):	Injectant (Cosolvent Nutrient Surfactant):	Comments
AL	N	N	Y	N		Reviewed a draft proposal for nutrients in soils.
AK	N	N	Y	Y	S	Surfactant used at a refinery to reduce iron-fouling at a recovery well.
AZ	N	N	Y	N		State Aquifer Protection Permit (APP) required; identical to Federal UIC regulations. New regulations may exempt UST sites from permit requirements.
AR	N	N	N	N		No experience yet. May require UIC and State discharge permit.
CA	N	N	Y	Y	S	No single State-wide authority; Regional Water Quality Control Boards have approval authority and may require a permit. UIC permit may also be required. Surfactant approved at CERCLA site; project halted for other reasons.
CO	N	N	Y	Y	N	UIC permit required. RCRA Corrective Action remedy including surfactants rejected. Nutrients injected at a CERCLA site.
CT	N	N	N	N		No experience yet. State permit required.
DE	N	N	N	N		No experience yet. Proposal being discussed at Dover AFB. Recent CERCLA ROD includes some enhancement to a pump-and-treat system as part of remedy.
FL	N	N	Y	Y	N	UIC permit required. Surfactants considered but not approved.
GA	N	N	Y	Y	N	UIC permit required. Some remediation sites include reinjection with nutrients.
HI	N	N	N	N		No experience yet. UIC permit required.
ID	N	N	Y	Y	C, N, S	UIC permit may be required. Co-solvent and surfactant injected in controlled cells.
IL	N	N	Y	N	N	State permit may be required. Surfactant proposal under review.
IN	N	N	N	N		No experience yet. Prior regulations made approval unlikely. New regulations under development should promote injection technologies.
IA	N	N	Y	Y	N	Most proposals rejected on technical grounds. Only nutrient injection (by EPA) approved.
KS	N	N	Y	Y	N	Permits issued at a fuel oil spill site.
KY	N	N	Y	Y	S	Surfactants demonstrated at CERCLA site.

5

Summary of State Policy and Experience with *In Situ* Ground Water Remediation (cont.)

State	Regulatory Prohibition (Yes/No):	Policy Prohibition (Yes/No):	Proposal Reviewed (Yes/No):	Injection Allowed (Yes/No):	Injectant (Cosolvent Nutrient Surfactant):	Comments
LA	N	Y	Y	N		UIC permit may be required. Proposals rejected on technical grounds, lack of containment.
ME	N	N	N	N		No experience yet. UIC permit required.
MD	N	N	N	N		No experience yet. Permit not required if containment of injectant is demonstrated.
MA	N	N	N	N		No experience yet.
MI	N	N	Y	Y	N, S	Surfactant injected had FDA approval (non-hazardous). Proposal must demonstrate injectant containment.
MN	N	N	N	N		No experience yet. State permit required.
MS	N	N	Y	Y	N	Program and UIC review required.
MO	N	N	Y	Y	N	Regulations prohibit injection that exceeds ground water protection criteria. Site-specific criteria may be used only for contaminated aquifers. For permitted projects, all injectant must be removed.
MT	N	N	Y	Y	N	Regulations being developed to allow short-term degradation during cleanup actions. State permit required.
NE	N	Y	Y	Y	N	Nutrient injection project failed. Subsequent surfactant proposal rejected. Will not approve new proposals on policy grounds.
NV	N	N	Y	Y	N, S	UIC permit required.
NH	N	N	Y	Y	N	Proposal must include recapture of injectant. Permit issued at a fuel oil site.
NJ	N	N	Y	Y	N, S	State Administrative Consent Order and Classification Exception Area designation may be required for non-CERCLA sites. Surfactant approval for small-scale field test that captured injectant.
NM	N	N	Y	Y	N	Discharge plan required as part of proposal.
NY	N	N	Y	Y	N	Nutrients injected at several sites.
NC	N	N	Y	Y	N	Closed systems have been allowed. Water quality permit required.

Summary of State Policy and Experience with *In Situ* Ground Water Remediation (cont.)

State	Regulatory Prohibition (Yes/No):	Policy Prohibition (Yes/No):	Proposal Reviewed (Yes/No):	Injection Allowed (Yes/No):	Injectant (Cosolvent Nutrient Surfactant):	Comments
ND	N	N	N	N		No experience yet. State Water Program followed by UIC program review.
OH	N	N	Y	Y	S	Surfactant field test approved for DNAPL treatment at CERCLA site. Project to begin Spring 1996.
OK	N	N	Y	Y	N	Program and UIC review required.
OR	N	N	N	N		No experience yet. UIC permit required.
PA	N	N	Y	Y	S	Surfactant pilot-scale study approved for remediating PCBs.
RI	N	N	N	N		No experience yet.
SC	N	N	Y	Y	N	UIC permit required. Allowed an infiltration trench rather than injection well. Will only approve closed systems.
SD	N	N	Y	Y	N	Allowed pilot study.
TN	N	N	Y	Y	N	Program office and UIC review. UIC permit application may be required.
TX	N	N	Y	Y	N, S	UIC permit required. Surfactant demonstration approved at RCRA facility for remediating carbon tetrachloride.
UT	N	N	Y	Y	N, S	UIC permit required. Surfactant demonstrations approved at a CERCLA site. Approval of surfactant at non-CERCLA site less certain.
VT	N	N	Y	Y	N	UIC permit required.
VA	N	N	N	N		No experience yet.
WA	N	N	Y	Y	N	UIC permit required if system is not closed.
WV	N	N	N	N		UIC permit required.
WI	N	N	N	N		No experience yet. Policy recently changed to allow injection for remediation. Program review required.
WY	N	N	Y	Y	N	UIC permit required.

7

Table 8. Summary of state policy of in situ groundwater remediation (EPA, 1996)

A comprehensive monitoring system must verify total removal of the injected substance. Table 8 summarizes state policies regarding the use of injection technologies. The column titled "regulatory prohibition" shows that no state has a total regulatory ban on injection. "Policy prohibition" means the state has or does not have policies that prohibit or discourage the use of injection technologies. "Proposal reviewed" means the state agency accepted for review a proposal that included injection and completed that review. "Injection allowed" means the State approved or failed to disapprove a proposal for injection or otherwise allowed the injection. "Comments" focus on the results of interviews with State contacts (United States Environmental Protection Agency, 1996).

The next five CERCLA performance criteria are balancing criteria. The performance of a remediation technology does not have to satisfy each of these criteria. Instead, the criteria are used as overall performance indicators, meaning that the selected technology must demonstrate the best overall performance relative to these criteria.

First, let's look at long-term effectiveness and permanence. This criterion is used to evaluate the ability of a proposed environmental remediation technology to reliably protect human health and the environment, after the clean up is completed. Relevant to this criterion are how permanent and complete the cleanup will be and what risks will be presented by the remaining contamination at the site. Cosolvent remediation performs well under this criterion. Since it is used to clean up the source of contamination, cosolvent remediation offers a permanent solution to cleanup environmental problems. The alcohol used in cosolvent flooding is also degradable. In field tests performed at Hill AFB, no alcohol was detected in the aquifer after three weeks (Enfield et. al., 1997)

The next criteria are reduction of toxicity, mobility, and volume through treatment. The objective of this criterion is to measure the degree to which the proposed remediation technology includes direct treatment of the contamination as opposed to containment or disposal elsewhere. This criterion presents some obvious overlap with the preceding criteria, however the focus here is more specifically on the residuals created after treatment. Cosolvent technology does well in one part of this criterion since the area of contamination is significantly reduced if not completely eliminated. However, the DNAPL is removed from the aquifer and still must be disposed of elsewhere, which is not preferred. Cosolvent remediation injects an alcohol that degrades rapidly. Most alcohols pose no long-term medical threats if consumed. The waste generated from removing the cosolvent-water-NAPL mixture from the aquifer would require treatment. If the alcohol is recycled, and the water is then placed into an air stripper followed by a granulated activated carbon system (GAC), the required treatment can occur at the contaminated site. The residual contamination would be contained on the GAC and would have to be destroyed or safely disposed of.

Short-term effectiveness is used to measure the risks posed to workers, the community, and the environment during the construction and implementation phases of the site remediation. Under this criterion, technologies favored are those that require a relatively uncomplicated construction process and short time to implement. Additionally, those technologies that pose the least disruption to the environment and can be easily monitored are favored. Cosolvent remediation minimally disrupts the environment since it can be easily adapted to an existing pump and treat system. The disruption of the environment due to the injection of alcohol can be localized and would not extend beyond

the treatment zone. Increasing the percentage of alcohol added to the aquifer also vastly decreases the time required to cleanup a site. Workers however, will be exposed to volatile chemicals that are extremely flammable (Lowe, 1996)

The objective of the implementation criterion is to measure the technical and administrative feasibility of the proposed remedy. Cosolvent remediation may require specialized equipment and labor depending on whether or not the alcohol is recycled. The main way to recycle alcohol is through distillation. Distillation systems require specialized manpower to set up and maintain. Equipment and materials are readily available. Since only a pilot scale test has been completed on this technology, implementation will require more time and monitoring until it is recognized as an accepted remediation technique. The pilot test at Hill AFB and the upcoming test at Dover AFB may help prove the feasibility of this technology.

The final balancing criterion is cost. Under this criterion, present values are calculated for all relevant costs over the multi-year period of the cleanup project. The objective of this criterion is to identify technologies that have reasonable costs, not necessarily the lowest one. As long as the technology is shown to be reasonable in cost relative to its effectiveness it may be selected over a technology that costs less overall. The EPA is careful to make this distinction because of the other important factors such as cleanup time that may be more critical to a decision than cost. The goal of this thesis is to determine whether cosolvent remediation can be cost-effective.

The final two criteria are modifying criteria. The purpose of these criteria is to ensure state and local issues that are not directly addressed in the threshold and balancing criteria are addressed. State acceptance is used to assess the degree to which cosolvent

remediation addresses any policy or administrative issue that the state may have. In general, state concerns tend to be with issues similar to those addressed in other area of the performance criteria. The state is likely to consider the technology's reliability, permanence, ease of implementation, and ability to meet ARARs (Skumanich, 1994). As noted earlier, cosolvent remediation technology is approved only in the State of Idaho.

The last criterion to be evaluated is community acceptance. This criterion measures the acceptance of the technology by the local community. It is likely that the performance of cosolvent remediation will be favorable if it performs well in other areas of the performance criteria. The community may be concerned with the reinjection of alcohol that contains small levels of contaminant in it. These levels change depending on the alcohol chosen. Community members may also have concerns over the introduction of a new substance, alcohol, which could pose health threats when used in large quanities as in alcohol flooding. The concern may be increased if the contaminated aquifer supplies drinking wells.

When selecting a technology to be used at a particular site, site managers generally do not use a rigorous or quantifiable method to balance the technology's ability to satisfy the CERCLA performance criteria. To be considered, a technology must clearly meet the two threshold criteria and be shown to perform adequately relative to the balancing and modifying criteria. Selection of a technology is largely based on the judgement of the site manager. In some instances, five point or other numeric rating scales may be used to summarize the performance of the technology relative to each of the criteria, but the ultimate determination is largely based on the site manager's professional judgement (Skumanich, 1994). Cosolvent flushing seems to be favorable

under most of the criterion developed by the EPA. This thesis will help with the cost determination. The biggest obstacle to using cosolvent flushing is the fear of injecting substances in the aquifer. If enough confidence and knowledge can be gained about how the cosolvent remediates DNAPLs, a state may be more willing to use cosolvent flushing as a remediation technology.

Chapter 3
Development of Model

3.1 Introduction

As discussed in Chapter Two, cosolvent flushing has potential to remediate a DNAPL source. The focus of this thesis is to determine if cosolvent flushing is a cost-effective alternative for site managers to apply. The software developed in this thesis gives potential users flexibility to input parameters that reflect their site specific situation. This chapter will discuss some of the details of the software that can be used to determine the cost of cosolvent flushing. In addition to cost, the software informs the user about the technology, and how CERCLA regulations interface with the technology. Lastly, the software provides the user with information about the successful field test of cosolvent flushing at Hill AFB. This chapter also serves as a user's guide for the software.

The software is programmed in Microsoft Visual Basic 6.0. Microsoft Visual Basic 6.0 was chosen for several reasons. First, it provided user-friendly interface. This allows the user to move around the program simply by clicking a mouse button. Visual Basic also has the ability to display graphics. These pictures can be shown to reinforce ideas being explained in the text. Visual Basic also has the ability to connect to other Microsoft products. It can be easily input into spreadsheets and databases, giving it flexibility to adapt to multiple needs. Lastly, Visual Basic can create executable files. The executable files run on any computer and the program does not require the user to have Visual Basic on their computer to use the program.

3.2 Cost Model

The main part of the software is a cost model that allows the user to calculate the cost of conducting a cosolvent flood. The model requests information concerning the following site parameters:

1. Target DNAPL contaminant
2. Alcohol being used to perform the cosolvent flood
3. Percentage of Alcohol being used (%)
4. Length of the DNAPL contamination (m)
5. Width of the DNAPL contamination (m)
6. Fraction of NAPL in pore space (%)
7. Mole fraction of the target DNAPL (0-1)
8. Hydraulic conductivity of the soil (cm/sec)
9. Distance from the surface to the water table (m)
10. Aquifer thickness (m)
11. Hydraulic gradient (m/m)

With this information the model goes through a series of calculations that can be broken into four major areas. In the first area, the model determines the number of wells needed to cleanup the contaminated area. As discussed in Chapter Two, the model calculates the maximum pumping rate of each well using equations 10-13 that assumes a maximum draw down of 30% of the aquifer thickness. Next, the capture zone width is calculated (equation 14). The capture zone width must be larger than twice the width of the DNAPL to ensure the DNAPL is adequately captured. If the contaminated area is larger than half the calculated capture zone width, the model breaks the area into smaller areas and a well pair is assigned to each area. The model assumes that only one area will be cleaned up at a time. After the number of wells is calculated, the model enters the second phase of calculations.

The performance portion of the model calculates the time required to cleanup a contaminated site. These calculations are based on Rao's solubility theory developed in

Chapter Two (Equations 2-3). The performance portion first calculates the mass of DNAPL in moles (Equation 4). Next, it determines the contaminant's solubility and the alcohol's cosolvency power (Equation 3 and 8). The model assumes the DNAPL will only solubilize and not mobilize which usually occurs at high alcohol percentages. The model then determines the time (Equation 9) needed to cleanup the area based on the pumping rate, the contaminant's solubility and the rate at which mass is removed (Equation 5).

The third portion of the model designs a distillation system to recycle the alcohol, using the design procedures developed in Chapter Two. This model determines the size of the distillation column using equations A-1 and A-3, and the number of plates necessary to separate the alcohol from the alcohol-water-DNAPL solution based on the flow rate into the column using equations 18-20. Once the column is specified the reboiler (Equations (A-13) - (A-17)) and condenser (Equation A-19) are sized. The amount of alcohol recycled is then calculated based on the alcohol chosen using equation (A-11) – (A-12). Since azeotropes occur at different percentages for different alcohols, the purity of the distillate varies with the alcohol chosen. After the amount of distillate is calculated, the amount of liquid to be disposed is determined (Equation A-21).

The last section is where the cost of cosolvent flooding is determined. In this section the capital and annual costs are determined. Capital costs include the cost of constructing the wells, distillation column (Equation (A-6) – (A-10)), reboiler (Equation A-13), and condenser (A-18). These costs are calculated based on size of the equipment. The software assumes that the equipment will last the entire lifetime of the project since cleanup times are usually less than a year. Capital costs also include the instrumentation

and contingency costs. Contingency costs were assumed to be 15% of the total capital costs, while instrumentation was assumed to be 5% of the capital costs. There is also an initial alcohol cost. Initial alcohol requirements are determined from the volume of contamination, the site's porosity and the percentage of alcohol being used (Equation 17).

The annual costs calculated are based on how long the equipment will be operated, determined by the time necessary to cleanup the source area. Often this is less than a year, and therefore the annual costs reflect only a fraction of the year the system is operating. If a project requires more than a year to clean up, the annual costs reflect the cost to cleanup a project per year. However when these costs are used to determine the total cost, they are multiplied by the estimated project length in years. Annual costs include the cost of utilities to operate the wells and distillation columns. The necessary utilities are steam, water, and electricity. Costs of these utilities are calculated based on Equations A-17, A-20 and 15-16, respectively. It was assumed that 15% of the plates within a distillation column require annual replacement due to wear on the column. In this section of the model, the additional alcohol that may be required to supplement the alcohol being recycled is also calculated (Equation 33). The total cost is then calculated based on the capital and annual costs of the project. The cost per kilogram of contaminant removed is also calculated along with the cost per volume of aquifer remediated.

3.3 Software

This section serves as a guide, allowing users to step through the software. The first screen the user will see is the introduction screen. This screen provides a generic

explanation of the objectives of the software. From the introduction screen, the user goes to the main menu (Figure 15).

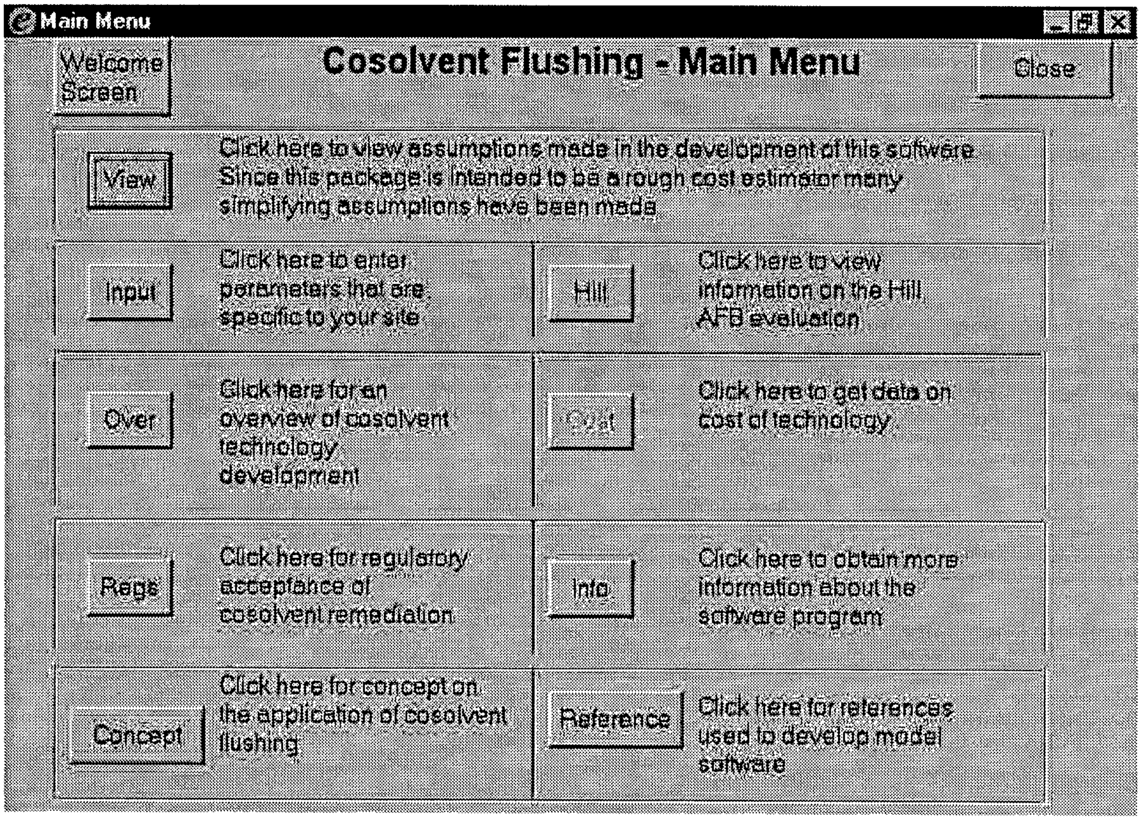


Figure 15. Software main menu

From this menu the user can view a number of screens by simply clicking on the appropriate button. A description of the screens that can be generated by clicking each button is given below.

If the user wants to view the assumption made in developing the cost model, the **View** button would be clicked. This informs the user of what assumptions are made in the model to determine flow rate, performance, and distillation column design. For example, the model assumes a homogeneous, isotropic site, and that the water-alcohol mixture completely contacts the DNAPL during flushing.

If the user would like to learn about the cosolvent flushing experiments performed at Hill AFB he or she would click on the **Hill** button. This screen describes the experimental conditions and the results achieved in the first cosolvent flood field experiment.

The **Over** button allows the user to learn about the history of cosolvent flushing. It details how the technology was developed by the petroleum industry to remove excess oil.

By clicking the **Regs** button, the user can view how CERCLA requirements apply to cosolvent flushing. The user can see the benefits and tradeoffs as they apply to the nine CERCLA criteria.

To obtain information about the development of the software package the user must click on the **Info** button. This button gives the user information on how to contact the model programmers if there is a problem or question about the model.

The **Reference** button lists all of the references used to create this model.

By clicking the **Concept** button, the user can view the general approach taken to construct each phase of the cost model. From this screen, the user can learn how the flow model, performance model and distillation model work.

To input data into the cost model, the user must click on the **Input** button. The cost button will not be usable until parameters are input. The screen then asks the user to select an alcohol and contaminant.

The model only allows the user to input one alcohol and target DNAPL at a time. Once they are input, the **Continue** button should be clicked. The screen as seen in figure 16 allows the user to input the remaining parameters:

1. Target DNAPL contamination
2. Alcohol being used to perform the cosolvent flood
3. Percentage of Alcohol being used (%)
4. Length of the DNAPL contamination (m)
5. Width of the DNAPL contamination (m)
6. Fraction of DNAPL in the pore space (%)
7. Mole fraction of target DNAPL (0-1)
8. Hydraulic conductivity of the soil (cm/sec)
9. Distance from the surface to the water table (m)
10. Aquifer thickness (m)
11. Hydraulic gradient (m/m)

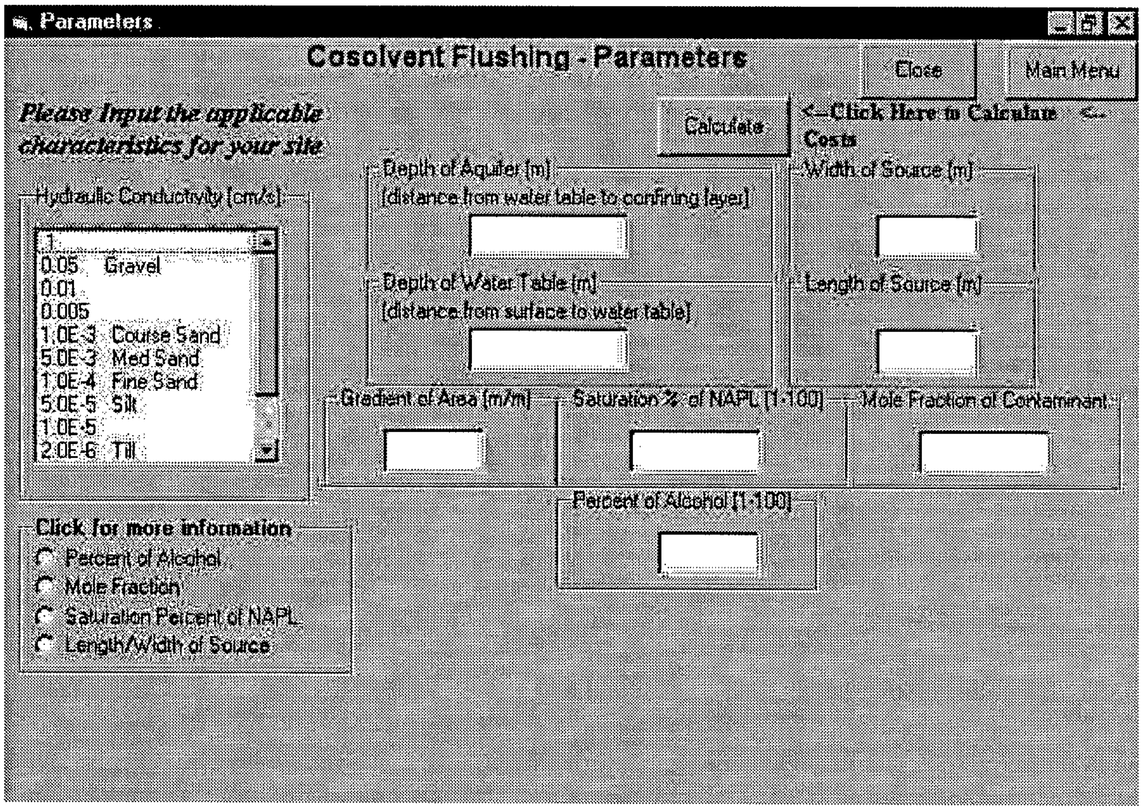


Figure 16. Model input screen.

This screen offers the users help in determining the percentage of alcohol to be chosen, percentage of saturation, the mole fraction of contaminant, and determining source dimensions. Once all parameters are input, costs are calculated by clicking on the **Calculate** button.

The **Cost** button is not available to the user until data is input into the model, however once this is complete the costs calculated can be viewed any time without having to re-input the data.

3.4 Sensitivity Analysis and Model Validation

A generic site was created to analyze how each alcohol performs when the percent of DNAPL saturation, percent of alcohol, hydraulic conductivity, and DNAPL type are varied. The parameters used to measure performance will be the time it takes to cleanup the source area, the total cost of the cosolvent flushing project, the cost per volume of contaminated soil remediated, and the cost per kilogram of contaminant removed. The generic site chosen is the same size site used by both Harwell and Lowe in the development of their cost estimates. This allowed the three estimates to be compared. The percentage of saturation of DNAPL was varied from 20 to 5%. This mimics the percentage at which cosolvent flushing remediation will typically be used. If the percentage of saturation exceeds 20%, it is more cost effective to remove the pool of contaminant and then use another technology to clean the remaining residual. The alcohol percentage varied from 90% to 10% in increments of 10%. This range was chosen since it mimics the highest concentration found in an alcohol flood, and the lowest percentage of alcohol currently experimented with while implementing cosolvent solubilization. The hydraulic conductivity was varied from 0.1 to 0.00005 cm/sec. If the hydraulic conductivity is lower than this, it is impractical to perform an alcohol flood. Varying the hydraulic conductivity over this range allows cosolvents to be applied in gravel soil as well as silty soil. The DNAPLs were varied among the 10 most common

DNAPLs found at sites across the country (Cherry and Pankow, 1996). This allows the user to see how cosolvent flooding changes when different DNAPLs are encountered. Table 4, in Chapter 2, provides a list of the DNAPLs being considered in this thesis.

In order to validate the model, the model was first run with the parameter values used by Lowe in his study (1996). A 1-acre site, having a contamination depth of 6 m was used. The site was assumed to have a porosity of 30%, and a DNAPL saturation percentage of 15%. The percentage of ethanol used to perform the cosolvent flood was 88%. TCE was used as the contaminant. Table 9 shows the results of the cost calculations of the model.

Capital (in $1,000's)		Annual (in $1,000's)	
Injection/Recovery Well	40	Steam Cost	1.3
Distillation Column	73	Water Cost	0.17
Reboiler	24	Plate Cost	0.65
Condenser	12	Well Operation	766
Instrumentation	7.5	Additional Alcohol	88
Contingency	22	Disposal	7.2
Initial Alcohol	1105	Maintenance	17
		Labor	53

Total **$2.2 M**

Table 9. Costs of 88% ethanol flood to remediate TCE.

Table 9 shows that the present value cost to remediate the aquifer with ethanol (including recycling) is $2.2M. This is somewhat less than Lowe's estimated cost of $2.7M for a 1-acre site which is expected since Lowe didn't include recycling in his estimate. Table 10 shows the cost estimate using the current model with recycling eliminated.

Capital (in $1,000's)		Annual (in $1,000's)	
Injection/Recovery Well	40	Steam Cost	0
Distillation Column	0	Water Cost	0
Reboiler	0	Plate Cost	0
Condenser	0	Well Operation	766
Instrumentation	7.4	Additional Alcohol	460
Contingency	22	Disposal	80
Initial Alcohol	1105	Maintenance	17
		Labor	53

Total **$2.6 M**

Table 10. 88% Ethanol-water system without recycling the alcohol.

Eliminating the recycling from the model raises the estimated cost of cosolvent flushing to almost $2.6M, virtually identical to Lowe's $2.7 M estimate. The time for remediation was calculated at 97 days, comparable to Lowe's estimate of 156 days. The results demonstrate that for the stated site recycling the alcohol lowers the overall cost of remediation by about 15%. Comparing tables 9 and 10, we can see that as long as the cost of the distillation system to recycle the alcohol does not exceed the cost of adding additional alcohol and disposing of the waste, it is cost effective to use recycling.

Chapter 4
Analysis

4.1 Scenario

The following baseline scenario was used to evaluate cosolvent flushing using the model developed in this thesis. The scenario assumed a contaminated area was distributed over 1-acre. The distance from the surface to the water table was assumed to be 3 meters, while the aquifer thickness was also assumed to be 3 meters. These distances are similar to those assumed by Lowe (1996) and Harwell et. al. (1995) in their cost estimates. The aquifer was assumed to have a porosity of 30%. Although TCE is the most common contaminant found on Air Force bases, it was not used in the generic scenario since not all of the alcohols can be recycled when TCE is the contaminant due to TCE's low boiling point. The DNAPL used to evaluate the model in the scenario was trichloroflouromethane since its other properties (molecular weight, solubility, and density) were the closest to TCE. Trichloroflouromethane's properties were midrange compared with the other DNAPLs evaluated in this thesis. Therefore it is assumed that costs estimtes for trichloroflouroemethane would be comparable to other DNAPLs under consideration. All five alcohols could also be recycled with trichloroflouromethane as the contaminant so that alcohol's performances could be compared. The percentage of the alcohol used is assumed to be 70% since this percentage was used in the experiments at Hill AFB. The DNAPL saturation percentage was assumed to be 15%. This means that 15% of the pore space in the aquifer volume contained trichloroflouromethane. Saturation percentages typically range between 20 and 5 %; 15% was chosen since it is

close to the saturation percentage used in Harwell's study. As trichloroflouromethane is assumed to be the only contaminant present, the mole fraction is 1.

Once the scenario was developed, a sensitivity analysis was performed on four parameters used by the model: DNAPL saturation percentage, hydraulic conductivity, alcohol percentage, and the type of DNAPL being remediated. These four parameters where chosen since they would be expected to have the biggest impact on cost and time to remediate a source area using cosolvent flushing. By looking at these parameters, we hope to determine what conditions are best for using cosolvent flushing.

4.2 Saturation Percentage

First, the DNAPL saturation percentage was varied from 20% to 5% to mimic the actual conditions under which cosolvent flushing will be used. As a reminder, the saturation percentage is the percentage of pore space that is filled by DNAPL. All other parameter values were kept the same as in the baseline scenario. As can be seen from figure 17, as the percentage of saturation increases the time to remediate the DNAPL also increases. This makes sense since if there is more contaminant present, the method should take longer to solubilize all of the DNAPL and clean up the area. The time differences between each of the alcohols can be attributed to the specific alcohol's cosolvency power. The higher the cosolvency power of the alcohol for the contaminant (in this case, trichloroflouromethane) the easier the alcohol can solubilize the DNAPL. For example, ethanol has the highest cosolvency power of 2.935, while TBA has the lowest cosolvency power of 2.5. The difference in cosolvency power between ethanol and TBA greatly affects the amount of time it takes to cleanup the DNAPL. As seen in figure 17, using TBA requires more than double the time required by ethanol to cleanup

up the same DNAPL because of the difference in cosolvency power. 1-Isopropanol and 2-Isopropanol have the same cosolvency power and therefore, there will be no difference in cleanup time between the two alcohols.

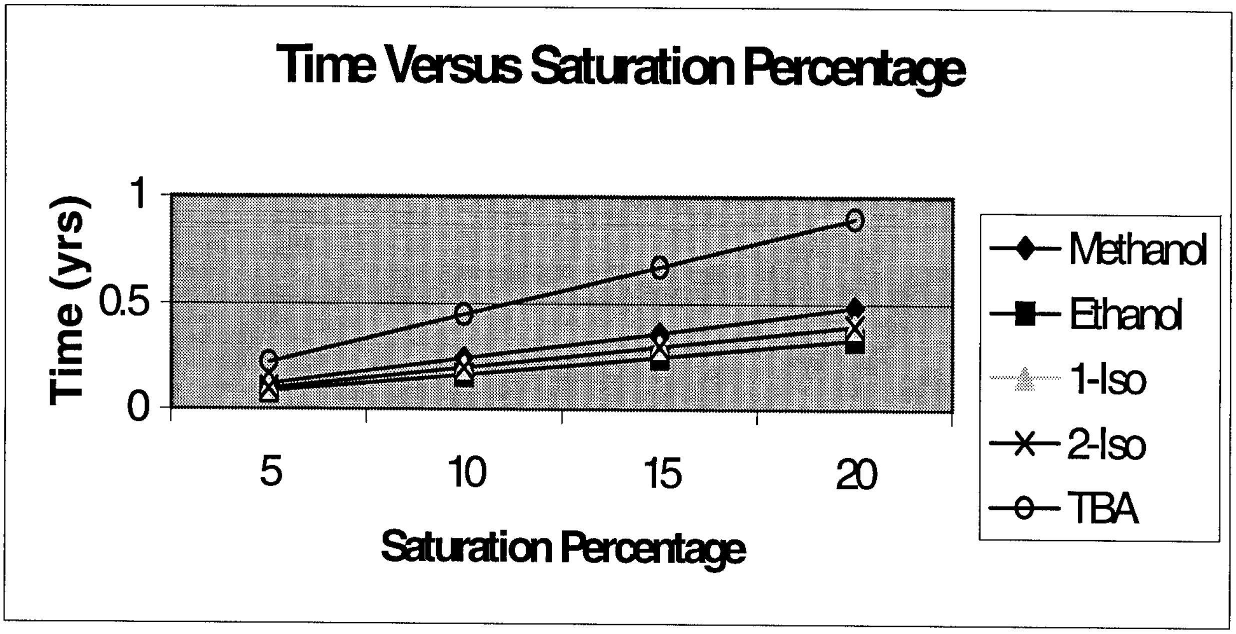


Figure 17. Time versus saturation percentage.

The saturation percentage also influences the total cost per kilogram of DNAPL cleaned. As the percentage of saturation increases the cost per kilogram of contaminant cleaned decreases. This is because we are removing more contaminant for the money spent. Although total cost of cleanup does increase as the amount of contaminant increases, the increase in cost is not as great as the increase in contaminant removed since certain fixed costs such as number of wells do not increase with the increase in contaminant saturation. As can be seen, in Figure 18, the cost per Kg at 5% saturation is about double the cost at 20% saturation.

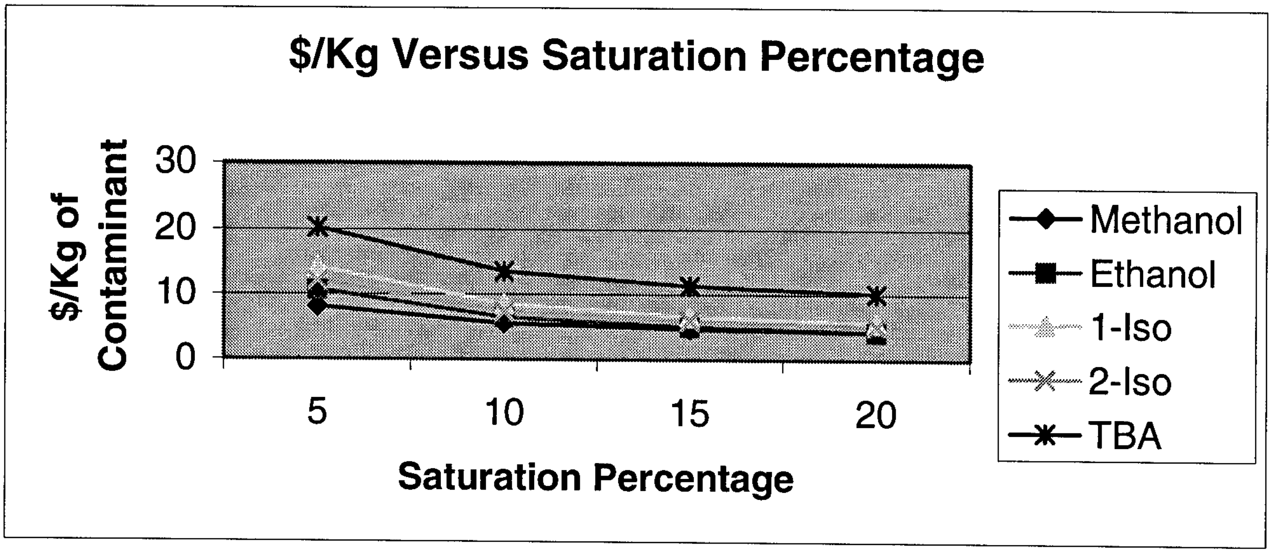


Figure 18. $/Kg of contaminant remediated versus saturation percentage.

It is apparent the largest decrease in $/Kg occurs when the saturation percentage increases from 5% to 10%. This is because the amount of contaminant present in the aquifer doubles, but the cost of remediating the aquifer only increases slightly as seen in figure 19.

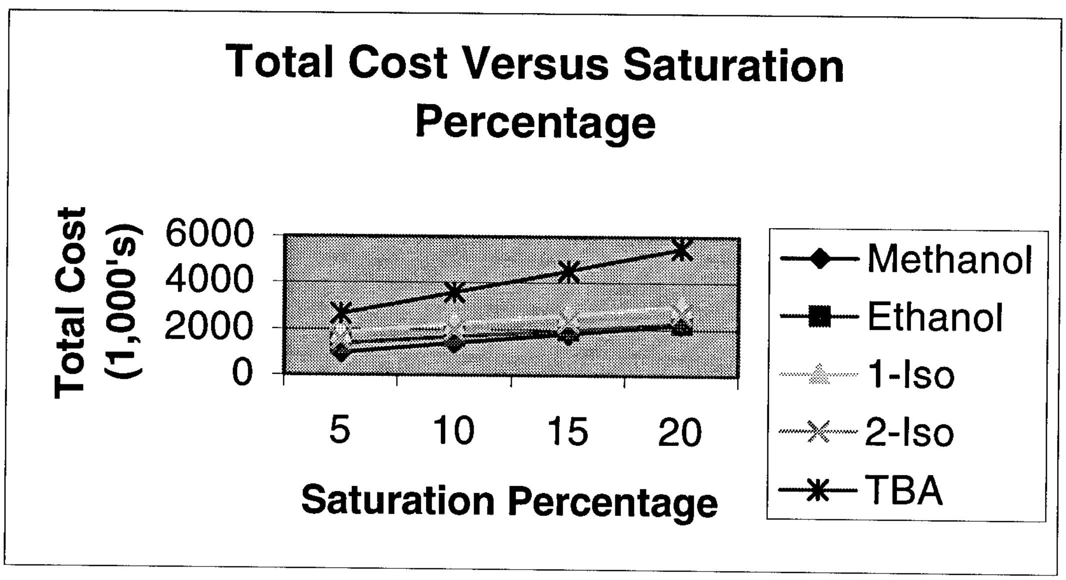


Figure 19. Total cost versus saturation percentage.

The total cost of remediation also increases with saturation percentage since more contaminant is present. As seen in figure 17 time and therefore cost, increase with increasing saturation percentage. Using methanol as an example, Figure 19 shows the total cost increases from \$1.0 M to \$2.2 M as the percentage of saturation goes from 5% to 20%. Figure 17 shows the increase in operating time from 44 days to 176 days. We can infer the operating cost quadruples (from \$408K to \$1.6M) which accounts for the increase in total cost. The differences in total cost among the 5 alcohols are due to two different factors, the cost of the alcohol and the cost of distillation of the alcohol. Methanol is the cheapest alcohol, but the cost to distill the alcohol is greater since it can be separated to 99.9% purity. In order for a distillation column to separate a liquid this well purely it must contain more plates than for an alcohol mixture that can not be separated as well. Ethanol can only be separated to 95% mole solution. Therefore, it does not incur the high distillation cost associated with building a distillation column with as many plates as required for methanol. There are however several drawbacks to this decrease in purity. One is that more ethanol must be added to the system since less will be recovered by the distillation column. Also, the quality of the ethanol is less. This could lead to some public concerns since the alcohol being re-injected back into the aquifer could contain a small portion of the DNAPL. 1-Isopropanol and 2-Isopropanol cost more than ethanol and methanol and can only be separated to 87% mole solution. This is not a very good separation and creates a substance that is not very pure, though it's fairly cheap to distill. TBA is the highest cost alcohol and therefore costs the most to use. Since it can only be separated to 88% mole solution, its distillation costs are similar

to 1-isopropanol and 2-isopropanol. The cost of each alcohol per gallon may be found in Table 3 in Chapter 2.

Let us now look at how cost per volume of contaminated aquifer changes as the DNAPL saturation percentage increases. The results of this comparison are intuitive, and maybe seen in figure 20. Since the total cost of remediation increases as the saturation percentage increases, but the aquifer volume to be treated remains the same, the cost per volume of soil increased linearly as the saturation percentage increased.

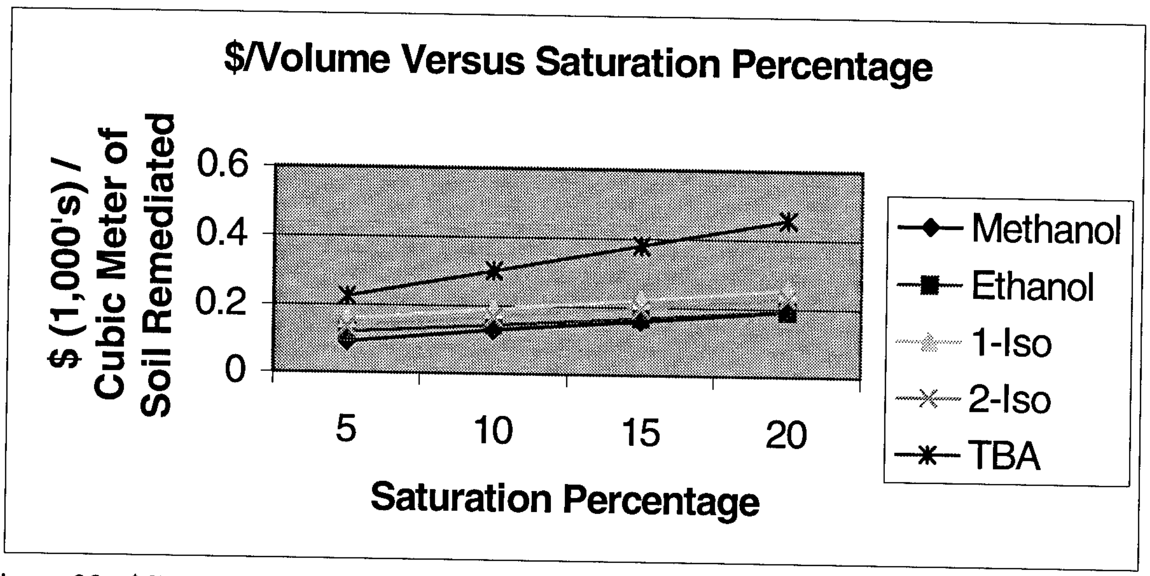


Figure 20. $/Volume versus saturation percentage.

In subsequent sensitivity analyses, we will focus on total cost and time, as cost per aquifer volume and cost per contaminant mass remediated are in large part reflected in the total cost of the remediation effort.

4.3 Hydraulic Conductivity

Varying the hydraulic conductivity demonstrates how cosolvent flushing will perform in different soil conditions. It is apparent from figure 21 that as hydraulic conductivity decreases the time required for remediating a site increases greatly.

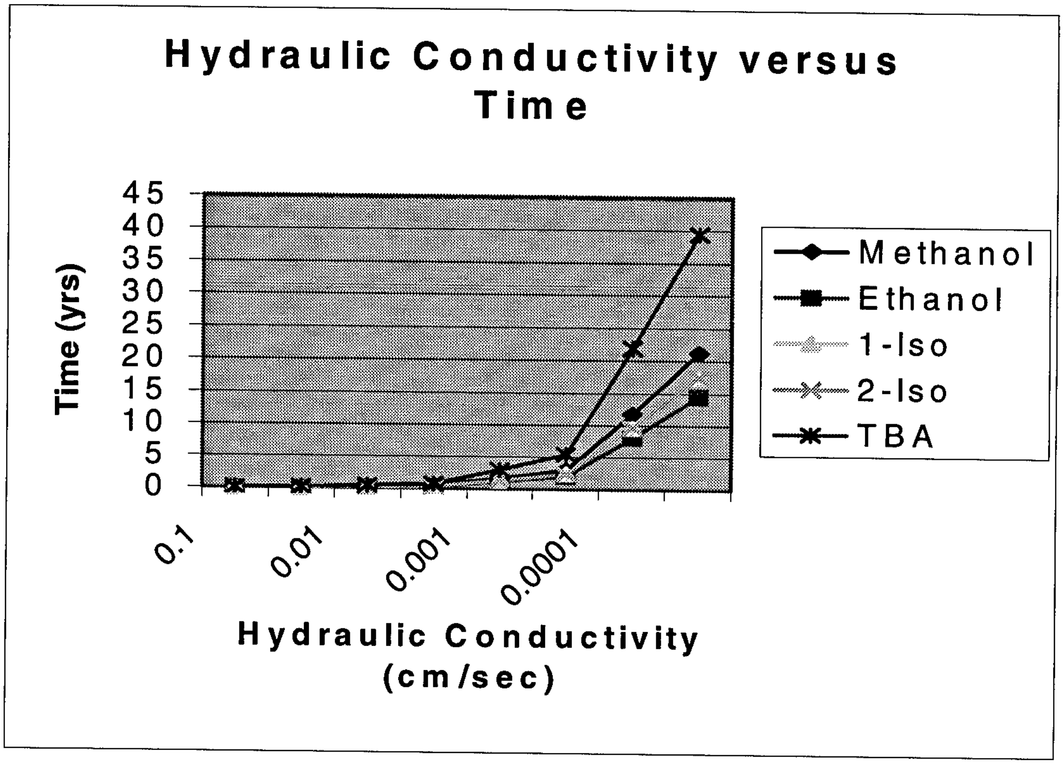


Figure 21. Hydraulic conductivity versus time.

As expected, the lower the hydraulic conductivity, the slower the cosolvent mixture flows through the aquifer, and the longer it takes to achieve cleanup.

Figure 22 compares total cost of remediation for different hydraulic conductivities. Interestingly, there appears to be a minimum total cost for all cosolvents when hydraulic conductivity is about .001 cm/s.

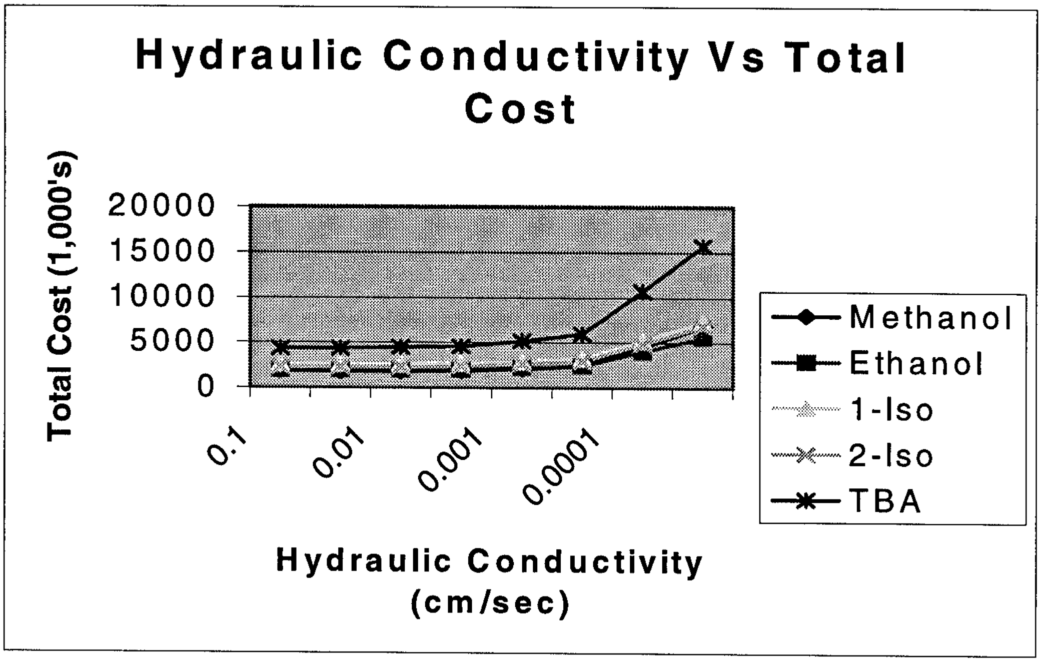


Figure 22. Hydraulic conductivity versus total cost.

The reason for this is not obvious since it has already been shown that as time increases the cost of remediating the aquifer also increases. However, when the hydraulic conductivity is varied, different parameters dictate the overall total cost. Ethanol is used as an example to illustrate this point. At a hydraulic conductivity of 0.1 cm/sec, the flow being pumped out of the aquifer is relatively large. In order to handle this flow, larger distillation columns are necessary to adequately separate the alcohol. The increase in distillation costs result in increased capital costs as seen in Figure 23. As the hydraulic conductivity decreases, the flow rate also decreases allowing the distillation and capital costs to decrease. However, the decrease in overall costs with decrease in hydraulic conductivity is only experienced until the increase in operating costs over time (due to longer times of operation) offset the decrease in capital costs. This occurs at a hydraulic conductivity of about 0.001 cm/sec.

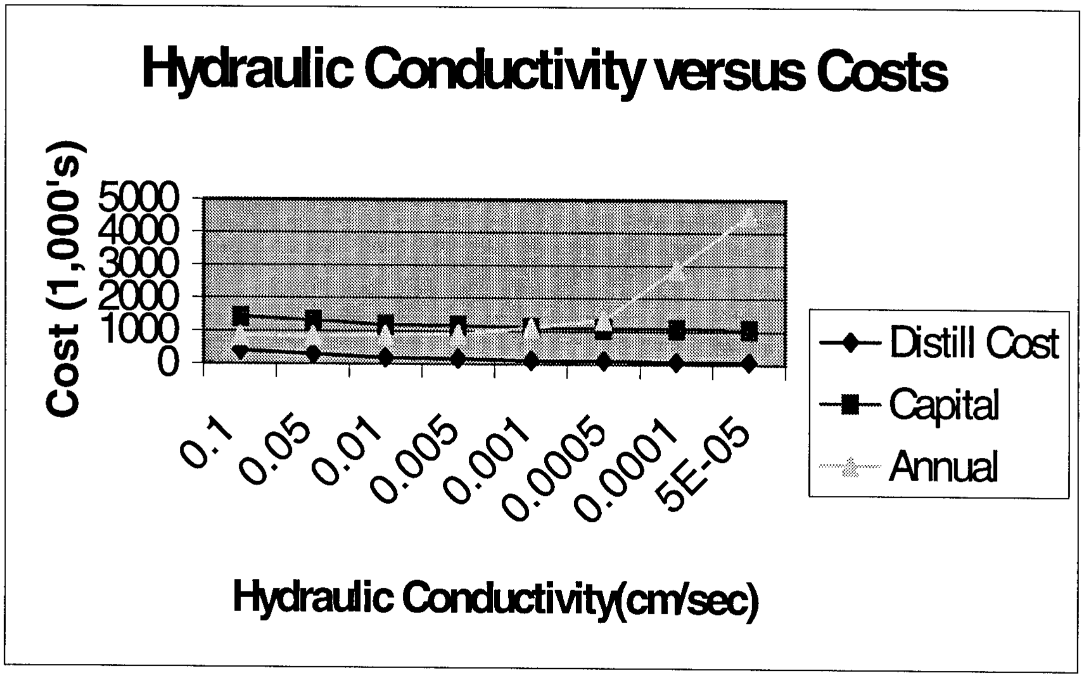


Figure 23. Hydraulic Conductivity versus cost using ethanol.

Since the cost of the distillation column has a large role in determining the total cost of the remediation, we ought to look at whether or not the soil's hydraulic conductivity affects the decision on whether or not the alcohol should be recycled. In order to compare whether or not an alcohol should be recycled, let's look at the costs associated with recycling the alcohol and assume the other costs such as well operation would remain the same whether or not the alcohol was recycled. If costs associated with distillation at a particular hydraulic conductivity exceed the cost of additional alcohol and disposal as a result of not recycling, it is no longer cost effective to recycle the alcohol. Included in the analysis are both capital and annual costs associated with recycling the alcohol. The first alcohol we consider is methanol, since it has the highest distillation costs due to its excellent ability to be separated. As illustrated in figure 24, as hydraulic conductivity decreases recycling of the alcohol should be considered since distillation

costs go down. However, due to the low cost per gallon of methanol and the high distillation costs associated with separating the alcohol, by the time it is cost effective to recycle the alcohol, it is no longer cost effective to use cosolvent remediation. This is because as hydraulic conductivity decreases to below 10^{-4} cm/sec, the time required to remediate the aquifer becomes exceedingly large (Figure 21)

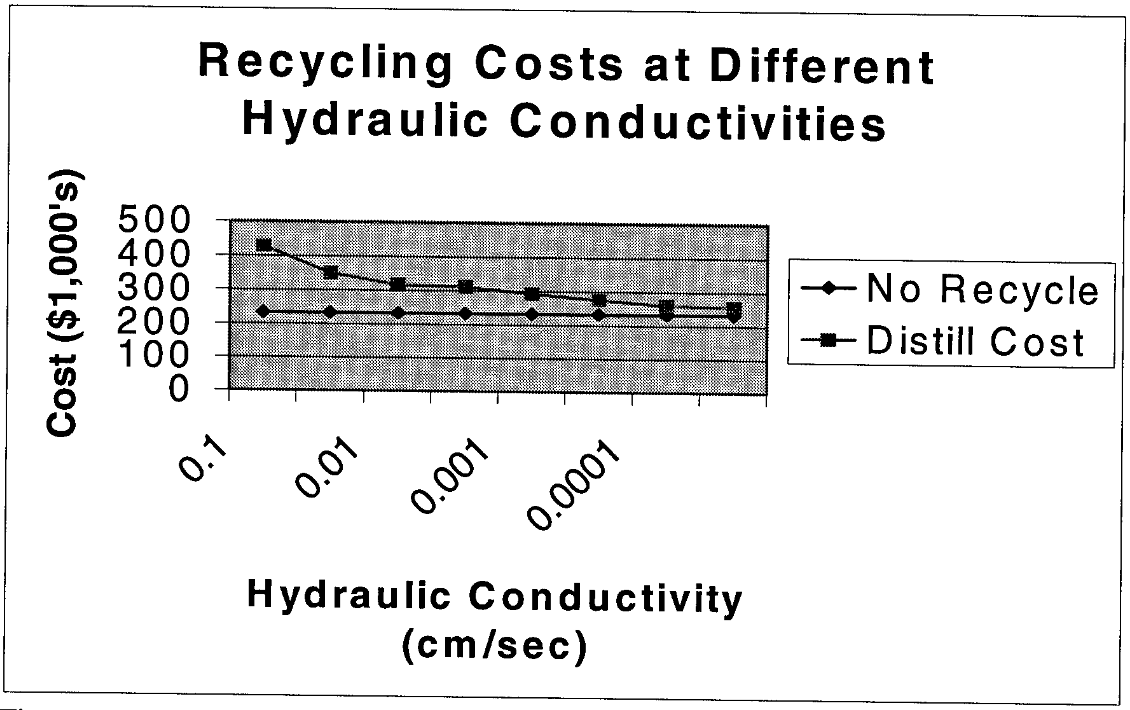


Figure 24. Methanol cost versus hydraulic conductivity.

Now let us consider ethanol recycling. Ethanol has the next highest distillation cost and the next lowest alcohol cost per gallon. As shown in figure 25, it is cost effective to recycle ethanol at any hydraulic conductivity. Given this information, it is safe to assume that 1-isopropanol, 2-isopropanol, and TBA can effectively be recycled at any hydraulic conductivity, since the distillation costs associated with the three alcohols are much lower than the distillation cost of ethanol. In addition to this, the cost of these

alcohols per gallon is also higher than ethanol. If the cost of the alcohol rises and the distillation cost decreases, it is advantageous to recycle the alcohol.

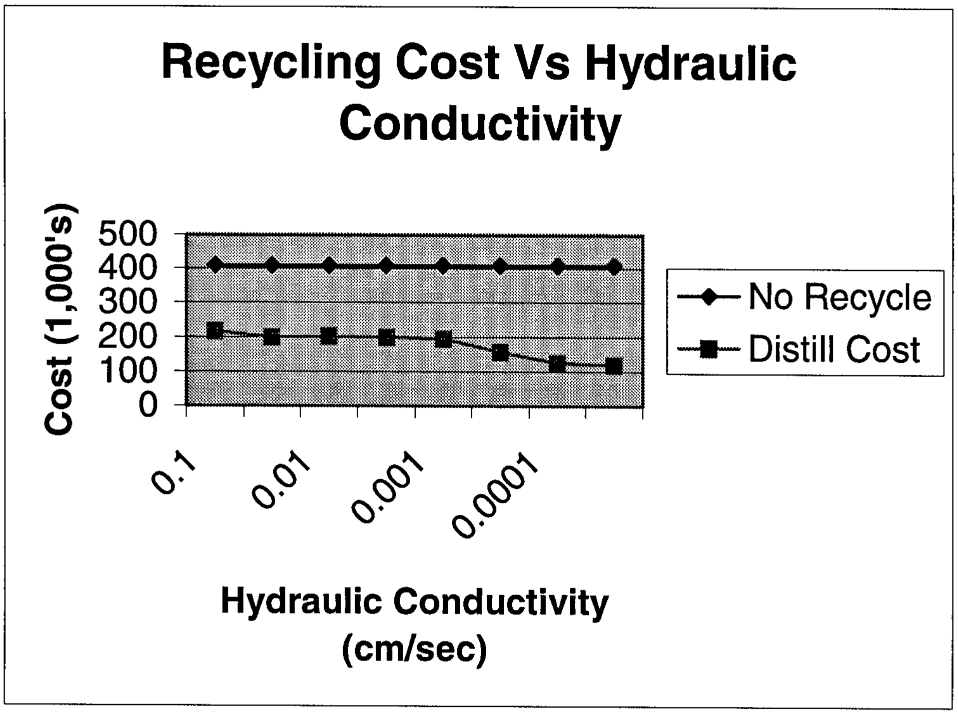


Figure 25. Ethanol cost versus hydraulic conductivity.

4.4 Percentage of Alcohol

The next parameter examined is the percentage of alcohol used. It has been shown in the literature that as the percentage of alcohol increases the time associated with cleaning up the contaminant decreases (Lowe, 1996). As demonstrated in figure 26, this is predicted by the current model. The reason the time decreases as the percentage of alcohol increases is due to the ability of the alcohol to solubilize more of the contaminant. As mentioned earlier, the difference in time between the alcohols to clean up the contaminant is due to the cosolvency power of the specific alcohol. One of the limitations of converting the McCabe-Thiele method of distillation design into a

computer model is that at certain percentages of alcohol, the model enters an infinite loop and doesn't provide a result. In figure 26, the model was unable to design a distillation column for 1-and 2-isopropanol and TBA when the alcohol percentage went below 35% and 38% respectively. The model also could not design a distillation column for ethanol when the percentage of alcohol was above 88% and below 28%. This is a limitation of the model.

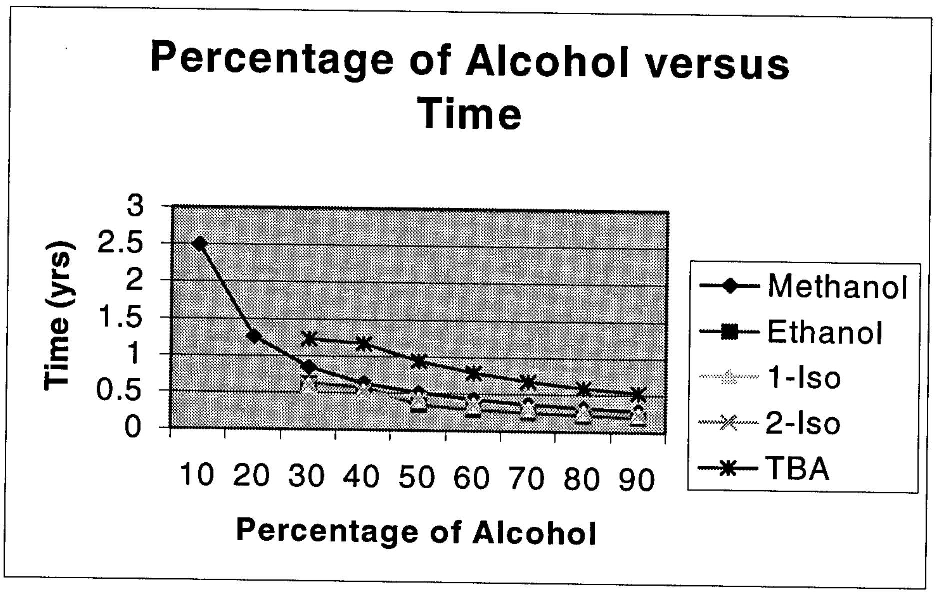


Figure 26. Percentage of alcohol versus time.

As the percentage of alcohol decreases, the operating costs needed to clean up the area will be higher since the time to clean up the areas increases. Also, as the percentage of alcohol decreases, the cost associated with distillation increases making it less cost effective to recycle the alcohol. The reason for this is because as the percentage of alcohol decreases, the effort required by the distillation column to separate the alcohol increase. This is because as the percentage of alcohol is further from the desired percentage of alcohol received from the distillation column, a larger distillation column is

required for the separation since more plates are required to separate the alcohol. Since more plates are required to separate the alcohol from the low percentage alcohol-water mixture, the cost to build and operate the column is greater.

This is true until the mixture being used is 80% to 90% alcohol. At this point the column must again be bigger. A large colmn is needed to adequately separate the mixture into distillate and bottom. If the column is not big enough, the alcohol mixture will simply flow through the column without being separated at all. Figure 27, which plots total costs versus alcohol percentage, is consistent with this explanation.

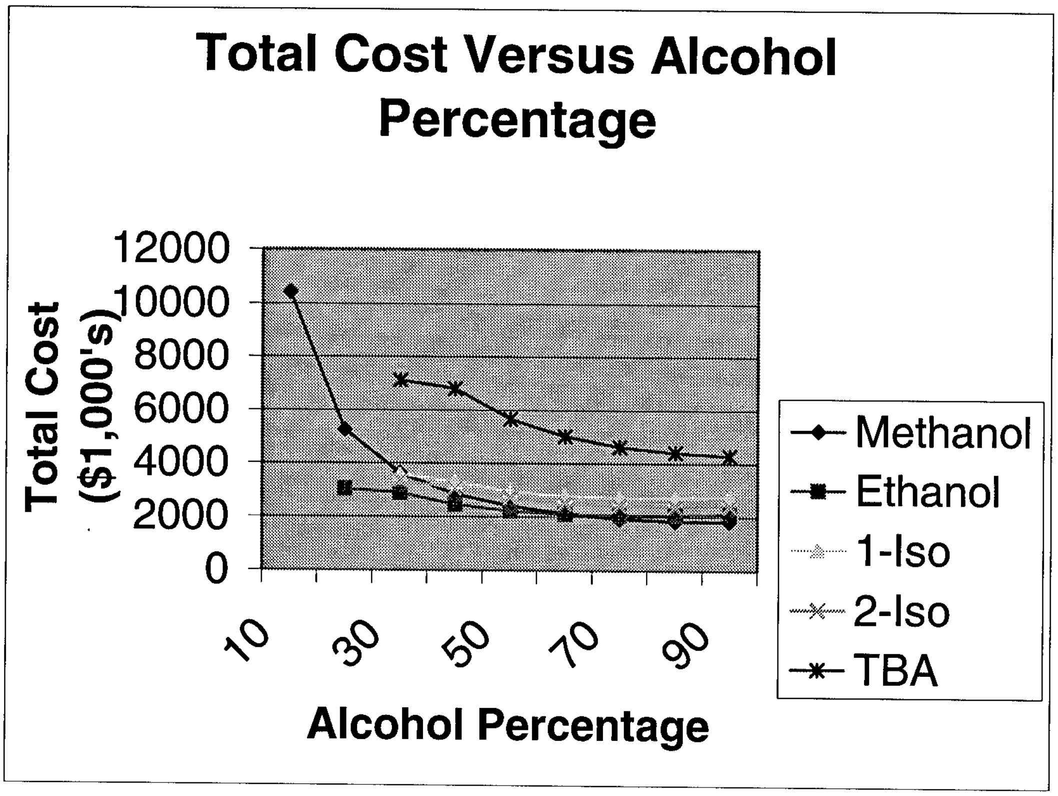


Figure 27. Total cost versus alcohol percentage.

The distillation costs are a large portion of the total cost when the percentage of alcohol used is low. Also, when a low percentage of alcohol is used, the costs associated with adding new alcohol to the aquifer is also low since not much alcohol is required.

Therefore, does it make sense to always recycle the alcohol? The decision to recycle or not depends upon several factors including the cost of the alcohol, cost of distillation, and disposal costs. As before, if the distillation costs exceed the cost of adding and disposing new alcohol it is not cost effective to recycle. Let's examine each alcohol individually to determine at what percentage it is cost effective to recycle.

The series of graphs in figure 28 display the costs associated with recycling and the costs that are incurred if the alcohol is not recycled for each alcohol considered in this thesis.

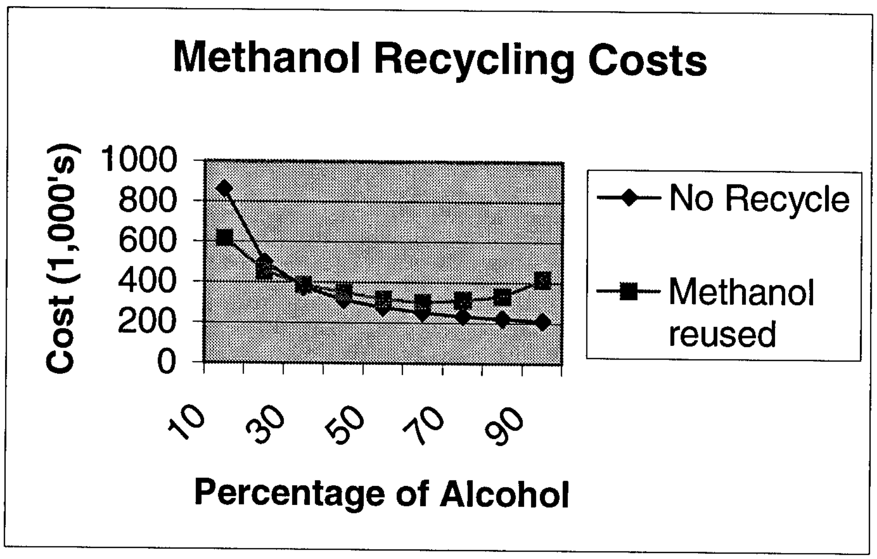


Figure 28a. Methanol costs.

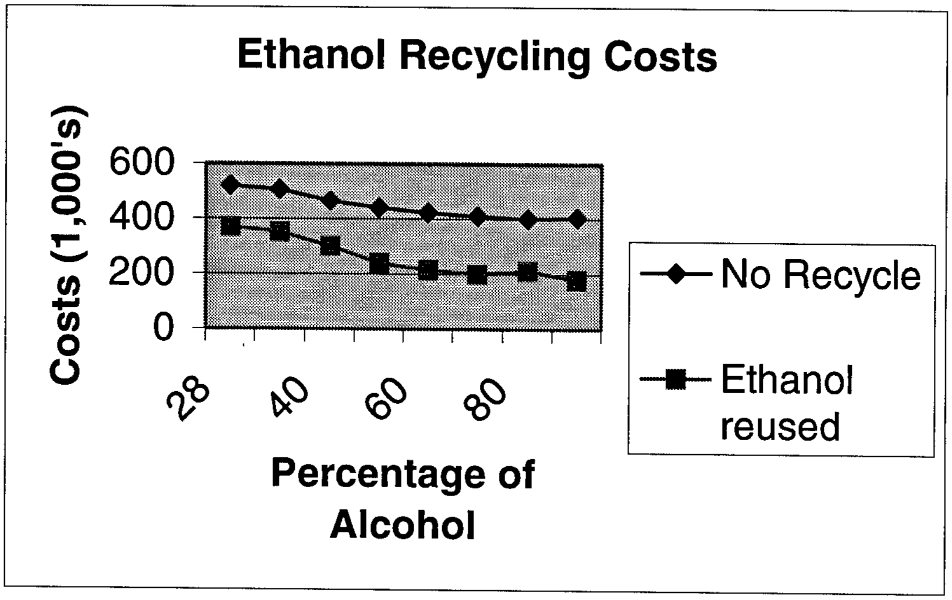


Figure 28b. Ethanol costs.

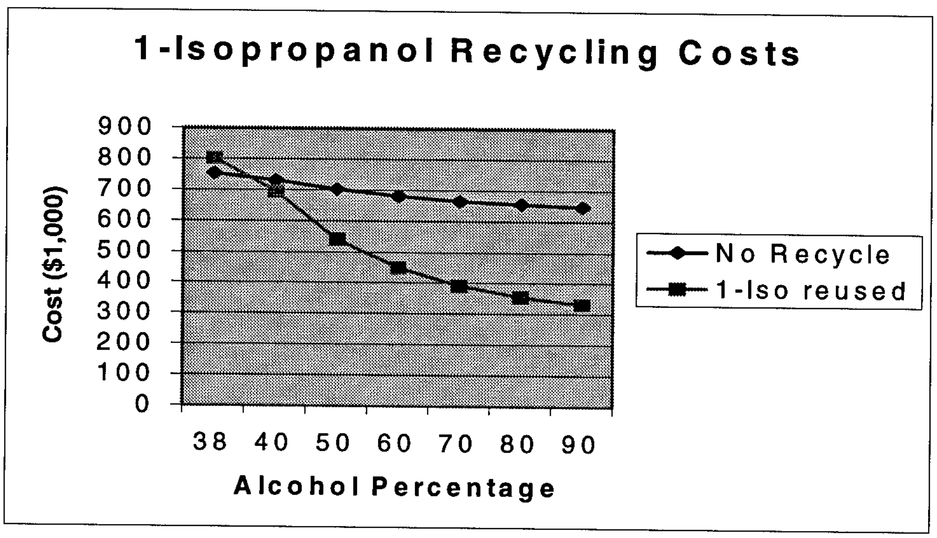


Figure 28c. 1-Isopropanol costs.

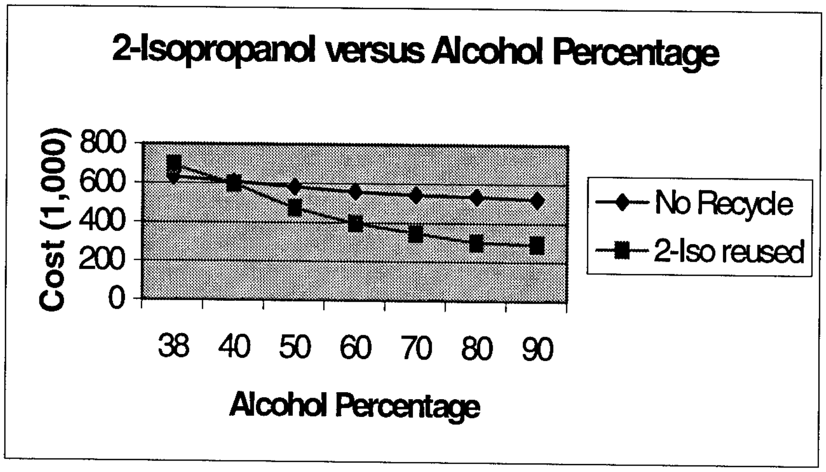


Figure 28d. 2-Isopropanol costs.

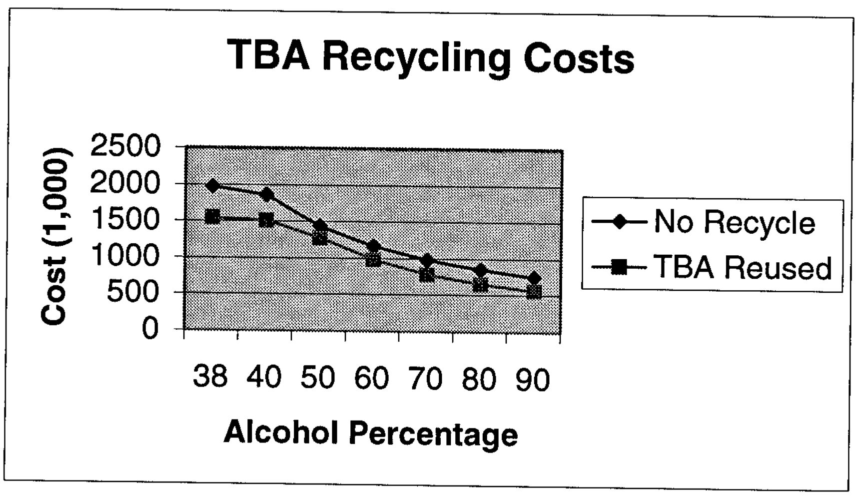


Figure 28e. Alcohol costs versus alcohol percentage.

As can be seen in figure 28a, it is only cost effective to recycle the alcohol when the percentage of methanol is below 30%. Above 30%, the cost to distill the alcohol is more than the cost to add new alcohol and dispose of the extracted mixture. Also note how recycling costs are minimum at alcohol percentages of about 70%, and that above

this percentage, costs begin to rise. This is due to the fact that the column needs to be bigger to achieve separation.

Figure 28c and 28d show that it is cost effective to recycle 1-Isopropanol and 2-Isopropanol when the percentage of alcohol in the mixture is above 40%. This is because percentages below 40% require large distillation columns. Also with recycle, there are considerable disposal costs because the distillation columns can only separate the mixture to 87% mole fraction. Ethanol and TBA should be recycled no matter what percentage of alcohol is being used to remediate the aquifer. As displayed in figures 28b and 28e, it is always more cost effective to recycle the alcohol than not to. TBA recycle is even cost effective at low percentages since the cost of TBA per gallon so high. Ethanol is also cost effective at all percentages because the alcohol can be separated more effectively, thus minimizing disposal costs.

4.5 DNAPLs

The last variable to be examined is how the cost and time to remediate a site using cosolvent flushing changes when different DNAPLs are encountered. The following list of ten DNAPLs was used to evaluate each of the alcohols (Cherry, 1996).

1. Chloroform
2. TCE
3. PCE
4. Carbon Tetrachloride
5. Trichlorofluoromethane
6. 1,1,1-TCA
7. Chlorobenzene
8. 1,2-Dichlorobenzene
9. 1,2-Dicholoroethane
10. 1,1,2,2-Tetrachloroethane

For several combinations of DNAPLs and alcohols, distillation is impossible since the contaminant's boiling point is lower than the cosolvent's. Therefore these DNAPLs will be evaluated assuming no recycling of the alcohol. If chloroform is the contaminant, none of the alcohols can be recycled using distillation. Methanol was the only alcohol that could be recycled if carbon tetrachloride, 1,1,1-TCA, and 1,2-Dichloroethane were the contaminants. Ethanol and methanol could only be recycled if TCE was the contaminant. All other contaminants could be remediated by all five alcohols, while allowing the alcohols to be recycled. Given this information, the computer model determines first whether or not the alcohol can be recycled, and then if it is cost effective to do the recycling. If it cannot recycle the alcohol due to the contaminant's boiling point or because it is not cost effective, the model will calculate the cosolvent flushing costs without recycling the alcohol. Given this information, a comparison can be made to determine which alcohol is best to remediate which contaminants.

As can be seen from figure 29a and 29b, the cost and the time required for remediating the site vary greatly with the contaminant. The factor that most influences these results is the contaminant's solubility. If the contaminant's solubility is high in the alcohol-water mixture (such as 1,2 Dichloroethane or 1,1,1 TCA), the time and cost of remediation is very low. This is because the contaminant solubilizes into the alcohol to a great extent. Other contaminants such as PCE have a very low solubility. This results in high costs due to long remediation times, as seen in figure 29a.

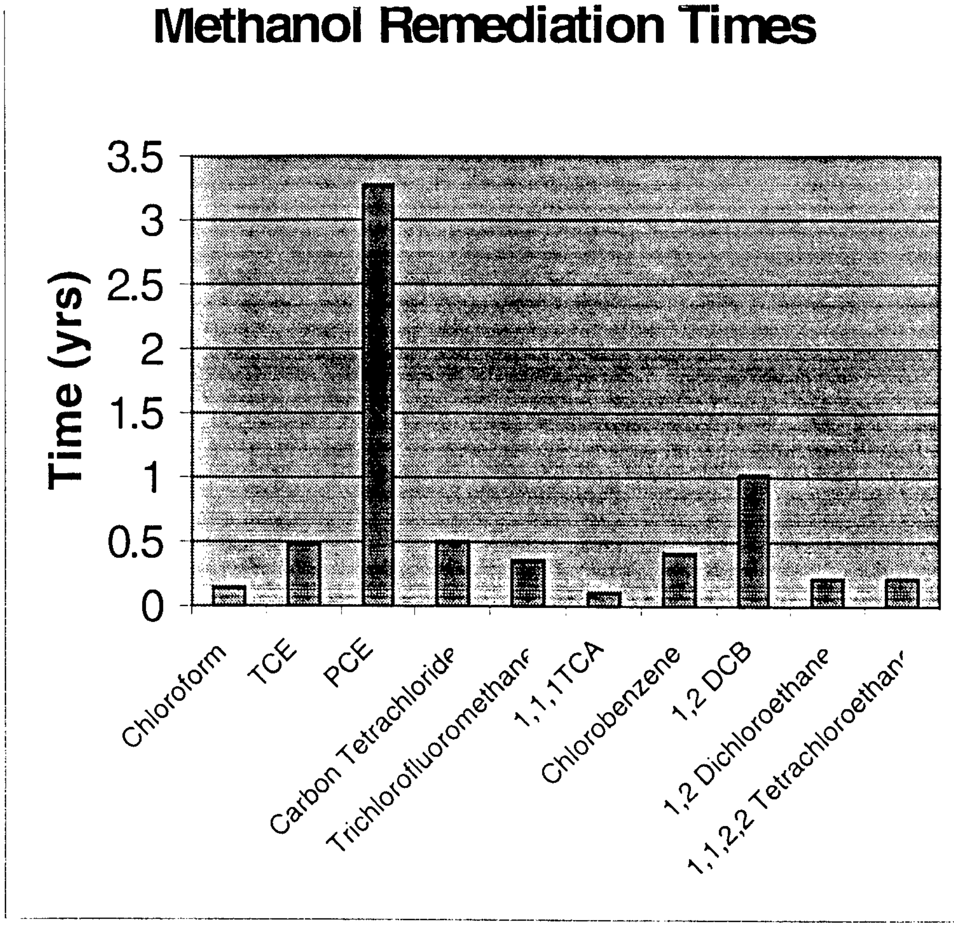


Figure 29. Total time to remediate varies DNAPLs using methanol

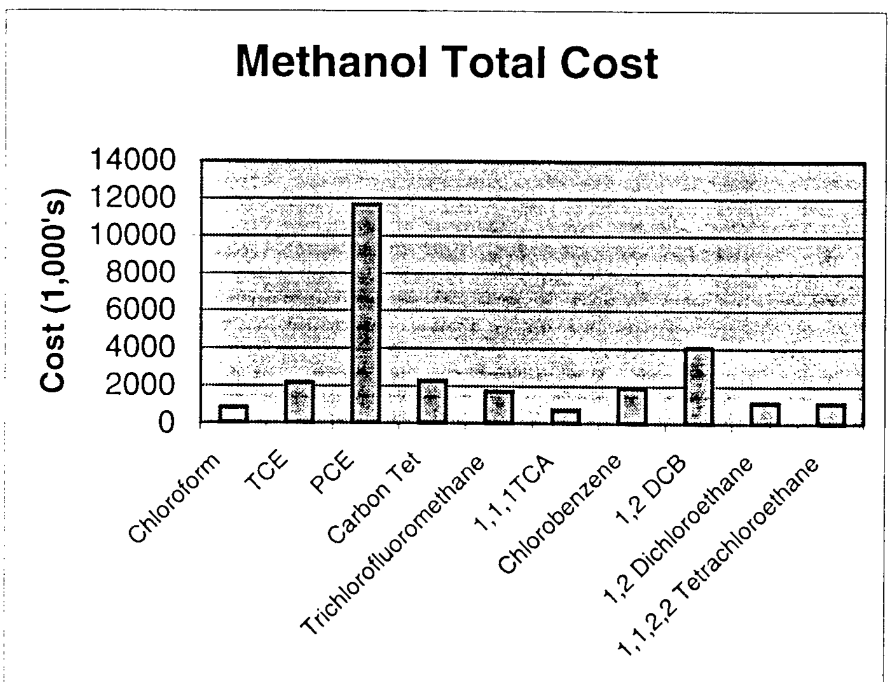
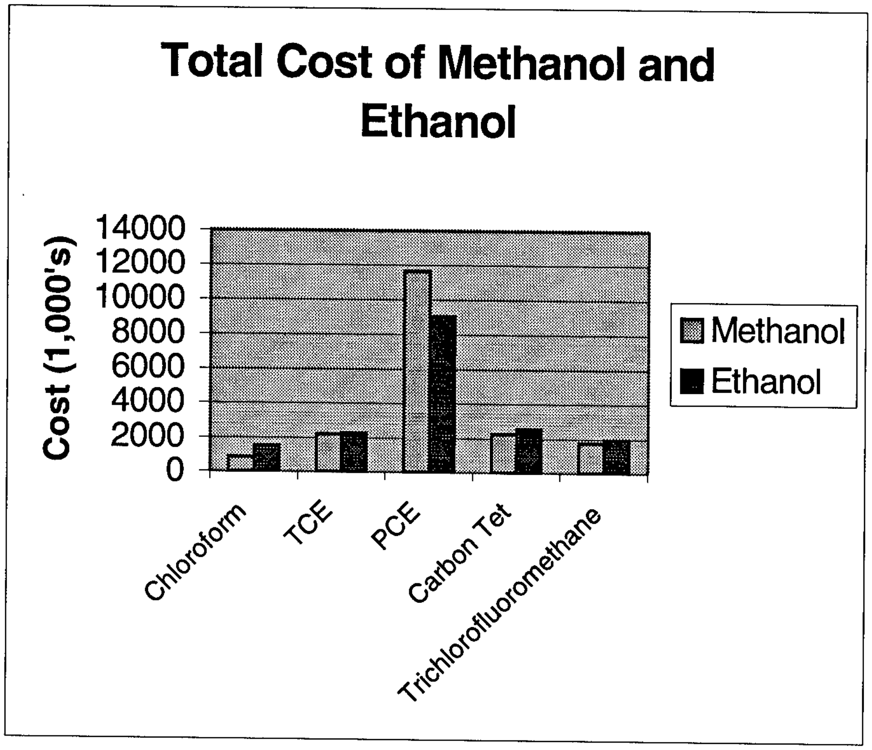


Figure 29b. Total cost to remediate varies DNAPLs using methanol.

The purpose of the model is to help users determine which alcohol is most cost effective in dealing with a target DNAPL. The first step to determining which alcohol is most effective is to eliminate as many alcohols as possible. Since 1-Isopropanol, 2-Isopropanol, and TBA have lower cosolvency powers and cost more than ethanol, it will always take these alcohols longer to remediate the aquifer when using identical percentages of cosolvent assuming solubilization of the DNAPL versus mobilization. This further increases the cost of performing a cosolvent flood, since the wells will be operating longer. Although the cost to build a distillation column for these alcohols is lower than the cost for methanol and ethanol, because azeotropes form at a much lower alcohol percentage, the distillation columns required for separation are smaller there cost savings are not enough to offset the high alcohol costs. This is particularly true since the distillation columns separate a smaller percentage of the alcohol so there is more of the alcohol-water mixture to be disposed of, resulting in higher disposal costs. Initial alcohol costs for 1-Isopropanol, 2-Isopropanol, and TBA are often greater than twice the costs of methanol, and 50% greater than ethanol. This makes it extremely unlikely that the three alcohols will ever be more cost effective than methanol or ethanol. Figures 19, 22, and 27 confirm this analysis. Based on this, in most cases the discussion of which alcohol to choose must be between methanol and ethanol. Figure 30 illustrates the cost differences between methanol and ethanol for the DNAPLs under consideration.



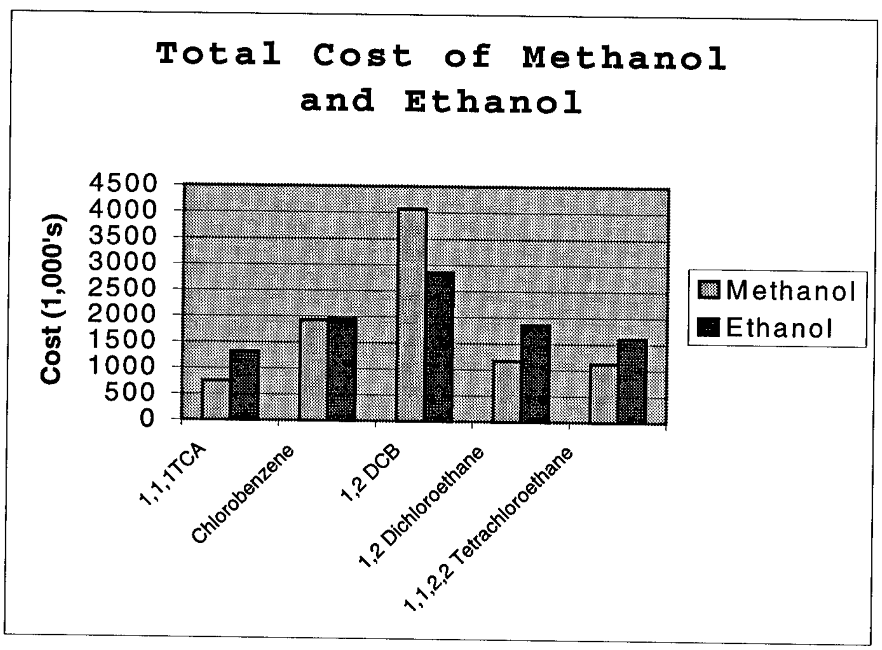


Figure 30. Cost comparison between methanol and ethanol.

As can be seen, it is more cost effective to use methanol if the contaminant present is 1,1,2,2-Tetrachloroethane, trichloromethane, or 1,1,1-TCA. The reason methanol is chosen over ethanol, for these three contaminants, is because both contaminants are very soluble, so clean up is relatively fast. Thus, the cheaper costs of methanol (approximately 1/3 of ethanol cost) make it the cosolvent of choice. For the less soluble contaminants (PCE or 1,2 Dichlorobenzene), this difference in cost if offset by the higher cosolvency power of ethanol and ethanol's ability to recover the distillation costs. The higher cosolvency power allows ethanol to remediate the contaminant faster than methanol. Since ethanol's system is operating less time, it incurs lower operating expenses. Less soluble contaminants however require more time overall to remediate than more soluble contaminants. This increase in time allows the distillation costs to be recovered by reusing the alcohol. Thus making it more feasible to recycle the alcohol. If the contaminant has mid-range solubility such as TCE or chlorobenzene, both alcohols have similar costs.

Simulations for the various DNAPLs showed that it was never cost effective to recycle methanol, while the ethanol was always recycled. The cost savings due to recycling can be demonstrated by looking at chloroform remediation. As shown in Figure 30, the ethanol flushing (without recycle) would cost double the methanol flood (without recycle). The main reason for this is the cost difference between the two alcohols. If the price of methanol increased to $.78/gal, it would be cost-effective to recycle methanol using a 70% alcohol mixture. If the price of ethanol drops per $.40/gal it would be cost effective to not recycle ethanol.

4.6 Cost Comparison between Cosolvent and Surfactant Flushing

Finally, let's compare the results of the current model to Harwell's estimate for surfactant flushing. Using Harwell's parameter values for a 1-acre site, the cosolvent model determined that to remediate the site using 88% ethanol solution would cost $2.1 M. Harwell estimated that surfactant flushing could remediate the site in 2 years for $1.9M. The cosolvent model presented in this thesis estimated the site could be remediated within 100 days, thus saving a significant amount of time.

Other factors besides time and cost that will impact a decision on whether to use cosolvent or surfactant flushing are (1) potential for downward mobilization of contaminant (Section 2.1.3.3), (2) toxicity of surfactant versus alcohols (Section 2.1.3.3 and 2.2.3), (3) regulatory acceptability (Section 2.6, Table 8), and (4) field experience using the technologies (Section 2.3).

Chapter 5
Conclusions and Recommendations for Further Study

5.1 Introduction

As engineers attempt to clean up aquifers contaminated with DNAPL, they face many challenges in deciding which remediation method to use. Cosolvent flushing offers managers an effective way to clean up DNAPL contamination. Cosolvent flushing can remediate an aquifer in a timely, cost effective manner. The model developed in this thesis calculates the total cost of cosolvent flushing, the cost per kilogram of contaminant remediated, the cost per volume of contaminated soil remediated and the time it takes to clean up the aquifer. These parameters can be used to help a site manager decide if cosolvent flushing is an effective option for his or her site.

5.2 Conclusions

Comparing results with results from Harwell's study (1995), the thesis showed that cosolvent remediation could be a cost effective alternative to surfactant flushing if the alcohol is recycled.

Applying the model parameters using the conditions of Harwell's study, the model determined the cost of cosolvent flushing to be $2.1M, while Harwell found surfactant flushing could remediate the site for $1.9M. However, cosolvent flushing could remediate the aquifer in less time than surfactant flushing, decreasing the time from the 2 years determined by Harwell to 100 days.

This thesis also determined it is not always cost-effective to recycle the alcohol. The biggest factor in determining whether to recycle alcohol or not is the cost of the

alcohol. If the cost of alcohol is low, as with methanol, it is only cost effective to recycle the alcohol when low alcohol percentages are used in the flushing solution. When the price of alcohol per gallon rises, it is more cost effective to recycle since the cost to distill the alcohol is less than the cost of additional alcohol plus the added disposal costs. The model found recycling ethanol and TBA was cost effective at any percentage of alcohol, while 1- Isopropanol and 2-Isopropanol were cost effective once the percentage of alcohol injected into the aquifer rose above 40%. It was also shown that as the percentage of alcohol used increased, the time and total cost required to cleanup the site decreased.

Hydraulic conductivity was important in determining how long cosolvent flushing would take to remediate a site. As the hydraulic conductivity decreased, the time required to remediate the aquifer increased as expected. This resulted in the cost of using cosolvent flushing to also increase dramatically.

The percentage of DNAPL saturation was also varied to determine its effects on the model's results. As expected the study found as the percentage of saturation increased the time and cost of cosolvent flushing also increased.

1-Isopropanol, 2-Isopropanol, and TBA were more expensive under all scenarios studied due to their costs, and need for increased disposal when compared with methanol and ethanol. They also took longer to clean up the DNAPL than methanol and ethanol. It was therefore concluded that 1-Isopropanol, 2-Isopropanol, and TBA should not be considered for cosolvent flushing no matter which contaminant is present. With these three alcohols eliminated, the cost efficiency of methanol and ethanol were compared using target contaminants. This comparison concluded that if the solubility of the

contaminant is high (i.e. 1,1,1 TCA) it is more cost effective to use methanol and not recycle the alcohol. If the solubility of the contaminant is low, such as PCE, it is more cost effective to use ethanol and recycle the alcohol. If the contaminant had a mid-range solubility such as TCE there is very little cost difference between using ethanol and methanol. Methanol always required more time to clean up the aquifer than ethanol since methanol has a lower cosolvency power than ethanol.

5.3 Recommendations for Further Study

In this thesis, a basic model was developed to determine whether or not cosolvent remediation is a cost effective alternative when the alcohol is recycled using solubilization. Given this basic model, the model can be developed further and made more complex. For example, additional contaminants could be added to the model. This will allow a user to manipulate the model to see if cosolvent flushing is a cost-effective alternative for a wider set of sites. In addition, the model could be expanded to model remediation of several contaminants at one time. Also, incorporating mobilization of the DNAPL into the model would add make the performance portion of the model more realistic when alcohol-water mixtures containing high alcohol percentages are used. This would make the model more realistic since rarely is only one contaminant present at a site.

As was demonstrated during the Hill AFB study, it may be effective to use multiple alcohols. The ability to simulate a flushing mixture containing several alcohols could also be incorporated into the model, with the model considering a distillation column that could distill each of the alcohols individually or simply the one with the

lowest boiling point. This model could also be validated using real cost data from Hill AFB and then applied to predict the results at Dover AFB, where the cosolvent will be recycled and the contaminant is PCE.

The final recommendation for further study is to create more models such as these for different emerging DNAPL source zone remediation technologies. A computer model is a quick and useful tool for a site manager to easily determine which technology is best suited to deal with his or her site specific problems within time and budget constraints. The more models that are available, the better the decision on which technology to use will be.

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Appendix

The plate cost may be determined by the diameter of the plates used. The plate diameter is calculated using the following equation.

$(Diameter)^2 = M_v*359*(460+T_b)*4/(60*492)*Pi*V_v$ (A-1)

$M_v = M_d(1 + R)$ (A-2)

$Q*(X_f) = M_d(X_d) + (Q-M_d)*X_b$ (A-3)

Where

Diameter = Plate diameter (ft)

R_{min}= Minimum reflux ratio

V_v = Vapor velocity at top of distillation tower (ft/sec)

M_v = Moles vapor per min at top of tower (lb-mol/min)

M_d = Moles of distillate/min (lb-mol/min)

M_b = Moles of bottom/min to be disposed (lb-mol/min)

Q = Pumping rate of well (lb mol/min)

The constants in equation 23 represent conversion factors.

The diameter is then converted to inches and the total cost of the plates is calculated based on the following formula (Peters and Timmerhaus, 1980).

If Diameter is less than 28 inches

Plate Cost = $1050*Number of Actual Plates (A-4)

If Diameter is greater than 28 inches

Plate Cost = $(37.5(Diameter) – 1050)*Number of Actual Plates (A-5)

These costs account for installation of the plates. This model assumes that 15% of the plates will have to be replaced annually (Peters, 1980).

Based on the number of plates required for distillation, additional distillation costs can be calculated. These costs include costs for plate covers, column shell requirements, and fittings. Fitting cost includes the cost for parts needed to connect the inlet flow, the reboiler, and the condenser to the distillation column. These costs are calculated using the following functions (Peters and Timmerhaus, 1980).

Plate Covers = ($80)*(Number of Plates +1)(Diameter) (A-6)

Shell Costs = 1.14523*(Steel) + 9691.31 (A-7)

Steel = Diameter*Height*(3/8)(1/144)*Pi*(490)*(1.12) (A-8)

Height = 2*(Number of plates) + 10 (A-9)

Fitting = (.02)(Total) (A-10)

Where

Diameter = Distillation diameter (in)

Steel = Amount of steel required to fit column based on weight of the shell

Height = Height of distillation column (ft)

Total = Total cost of distillation column including shell, plates and plate covers

This model assumes the density of steel is 490 lb/ft^3. A shell wall thickness of 3/8-inch steel will be used. The distillation column skirt is 10 ft high, and each plate is 2 feet tall.

Once the cost of the distillation column is calculated, the model calculates the amount of alcohol distilled, and sizes the reboiler and condenser. It then calculates the cost associated with these items. The amount of distilled alcohol is calculated to determine if additional alcohol must be added to the aquifer and the cost of additional alcohol required.

$$AddAlcohol = Q_{alc}*Percent_a*Time_{op}*Cost_a \quad (A-11)$$

$$Q_{alc} = Q*Percent_a - Q_{dis} \quad (A-12)$$

Where

AddAlcohol = Cost of adding additional alcohol ($)

Q_{alc} = Additional alcohol required (gal/min)

$Time_{op}$ = Annual time system is operating (min)

$Cost_a$ = Cost of the alcohol ($/gal)

Q = Pumping rate of well (gal/min)

Q_{dis} = Rate the alcohol is being distilled (gal/min)

The size of the reboiler and condenser is based on the amount of liquid being distilled by the column. The cost of the reboiler is calculated using the following equation developed from Peters and Timmerhaus (1980).

$$ReboilerCost = 8.15625*ReboilArea + 9093.75 \quad (A-13)$$

$$ReboilArea = Reboil/(80)(358-212) \quad (A-14)$$

$$Reboil = ((H_v-H_l)*M_v)+(M_b(212-T_b)*c_{pl})- (Feed*(Feed_b - T_b)*c_{pl} \quad (A-15)$$

$$Feed_b = (X_f*T_b)+ (1-X_f)*212 \quad (A-16)$$

Where

ReboilArea = Area over the reboiler the distillate is distributed (ft^2)

Reboil = Rate of heat transfer (Btu/min)

$Feed_b$ = Temperature the distillate is heated to (F)

M_d = Moles of distillate/min (lb-mol/min)

M_b = Moles of bottom/min to be disposed (lb-mol/min)

$H_v - H_l$ = Latent heat of the mixture (BTU/lb-mol)

c_{pl} = Heat capacity of the mixture (BTU/lb-mol-F)

X_f = Mole fraction of alcohol to be distilled

T_b = Boiling point of alcohol (F)

This model assumes the coefficient of heat transfer in the reboiler is 80 BTU/min(ft^2)F, 358 degrees F is the temperature of steam, the bottom liquid (water) boiling point is 212 F.

Once the size of the reboiler is established the cost of steam required to operate the reboiler can be calculated using the following equation (Peters and Timmerhaus, 1980).

$$\text{Steam Cost} = (\text{Reboil}*\text{Hour}_{op}*.\text{Steam}_c*60)/(915.5) \quad \text{(A-17)}$$

Where

Steam Cost = Annual cost of steam to operate reboiler ($/yr)

Reboil = Rate of heat transfer (Btu/min)

$Hour_{op}$ = Annual time reboiler is operating (min)

$Steam_c$ = Cost of steam ($/lb)

This model assumes the cost of steam is .75/1000 lb. It also assumes the heat of condensation is 915.5 Btu/lb.

Finally, the model calculates the condenser costs. These include the cost of the condenser, the annual cost of operating the condenser, and the disposal cost of the bottom liquid.

Like the reboiler the model evaluates the cost of the condenser based on its size (Peters and Timmerhaus, 1980).

$$CondenseCost = 6.375*(HeatArea) + 4650 \quad (A-18)$$

$$HeatArea = M_v*(H_v-H_l)/(T_b-80)*100 \quad (A-19)$$

Where

CondenseCost = Cost of the Condenser ($)

HeatArea = Heat transfer area of the condenser (ft^2)

M_v = Moles vapor per min at top of tower (lb-mol/min)

$H_v - H_l$ = Latent heat of the mixture (BTU/lb-mol)

T_b = Boiling point of alcohol (F)

This model assumes the feed temperature is 80 F, and the coefficient of heat transfer in the condenser is 100 Btu/min(ft^2)F.

Next, the cost of the annual cold-water requirement to operate the condenser is calculated.

$$CWater = (M_v*(H_v-H_l)*(Cost_w)*Hour_{op})/Temp_w*Cp_{lw} \quad (A-20)$$

Where

CWater = Cost of cold water ($/yr)

M_v = Moles vapor per min at top of tower (lb-mol/min)

$H_v - H_l$ = Latent heat of the mixture (BTU/lb-mol)

$Cost_w$= Cost of cold water ($/lb)

$Hour_{op}$ = Annual time condenser is operating (min)

Cp_{lw}= Heat capacity of water (Btu/lb-F)

$Temp_w$= Temperature of cooling water

This model assumes the temperature of the cooling water is 50 degrees F, and the cost of cold water is \$.054/10,000 lbs.

Finally, the disposal cost of the bottom liquid can be calculated using the following equation.

$$\text{Disposal} = Q_d * \text{Cost} * \text{Trip} \tag{A-21}$$

Where

Disposal = Cost of disposing waste (\$/yr)

Q_d = Bottom liquid in distillation column to be disposed (gal/yr)

Cost = Cost to dispose hazardous waste (\$/mile-gal)

Trip = Distance traveled to dispose hazardous waste (miles)

This model assumes the cost of disposal is \$15.98 per 6,000 gallons. This cost was obtained using Remedial Action Cost Engineering Requirements System (RACER). The model also assumes the distance traveled to dispose the hazardous waste is 100 miles.

Since the time needed to remediate the aquifer was often less then 1 year, a discount rate was not used. It was also assumed that the capital equipment would not be replaced since the total project time was again less than 1 year. All capital costs include equipment requirements, initial alcohol requirements, and overhead costs. These were considered one-time costs that occur during the projects lifetime. Annual costs were the costs that had to be paid while the cosolvent flushing system was operating. Annual costs such as well operation were multiplied by the amount of time the system was operating annually. If these operations occurred over several years, the annual operating cost only calculated one year, however the total cost of the project accounted for the entire length of time the project would be operated.

Vita

Captain Stacey L. Anason was born on 6 December 1970 in Appleton, Wisconsin. She graduated with a Bachelor of Science in Civil Engineering from the United States Air Force Academy in May 1993. Upon graduation, she received a regular commission in the United States Air Force.

She was first assigned to the 50th Civil Engineer Squadron, Engineering Flight, at Falcon Air Force Base, Colorado as the Chief of Programming. Within a year, she became a site support engineer for four worldwide satellite locations.

In June of 1995, she was assigned to the 64th Civil Engineer Squadron, Readiness Flight at Reese Air Force Base, Texas as the Flight's Commander. Upon notification of the base's closure, she was chosen to head closure operations for the Civil Engineering Squadron. In May 1997, she became the Base Civil Engineer thus allowing her to fully implement base draw down and closure plans.

In September of 1997, she entered the School of Engineering at the Air Force Institute of Technology. Upon graduation, she will be assigned to the 7th Air Force, Republic of South Korea, as Chief of Readiness Operations.

Capt Anason is married to Capt David Anason of Plymouth, Michigan. They have one son, Tony 3.

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13. ABSTRACT *(Maximum 200 words)*

Dense non-aqueous phase liquids (DNAPLs) in the zone beneath the water table can be a virtually permanent source of groundwater contamination that cannot be remediated by currently available technologies. Cosolvent flushing is a new technology that has the potential to remediate these sites and could pose a solution to the problem of DNAPL source areas.

A computer model was developed to determine the cost and time to remediate an aquifer using cosolvent flushing. Included in the model is a module to calculate the costs of recycling the alcohol that is used as the cosolvent. The model was validated using site conditions to a prior study. It was determined that recycling the cosolvent allows cosolvent flushing to be a cost effective alternative to surfactant flushing, another new technology being considered for DNAPL source remediation.

Sensitivity analysis of the model was conducted by varying the saturation percentage of contaminant, percentage and type of alcohol used in the cosolvent mixture, site hydraulic conductivity, and the contaminant. Five alcohols were modeled: methanol, ethanol, 1-isopropanol, 2-isopropanol, and tert-butyl-alcohol (TBA). 1-Isopropanol, 2-isopropanol, and TBA were always more expensive than methanol and ethanol. Methanol was found to be more cost-effective when used on DNAPLs with high solubilities, while ethanol was found to be more cost-effective when used on DNAPLs with low solubilities. Methanol always took longer than ethanol to remediate the source area since methanol had a lower cosolvency power.

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